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STUDIES ON THE NATURE OF THE RACEMIC MODIFICATIONS OF OPTICALLY ACTIVE COMPOUNDS IN THE SOLID STATE

Part VI. The Nature of the Racemic Modifications of 3-Nitro-*p*-toluidino-, 5-Iodo-*o*-toluidino-, 4-Nitro-*o*-toluidino-, Oxy-, 2-Nitro-*p*-toluidino-, 3-Nitro-4-chloroanilino-, 2 : 5-Dichloroanilino- and 4-Chloro-*o*-toluidino-methylenecamphors

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Received February 24, 1947

In this paper we have described our investigation of the nature of the racemic modifications of oxymethylenecamphor and its condensation products with 3-nitro-*p*-toluidine, 5-iodo-*o*-toluidine, 4-nitro-*o*-toluidine, 2-nitro-*p*-toluidine, 3-nitro-4-chloroaniline, 2 : 5-dichloroaniline and 4-chloro-*o*-toluidine.

A racemic modification may exist in the solid state in one of the following three forms: (1) a mechanical mixture (conglomerate) of the *d*- and *l*-forms; (2) a true racemic compound of the *d*- and *l*-forms; and (3) a solid solution (mixed crystal) of the optically active and opposite forms.

Three methods have been devised for determining the nature of the racemic modification. Two of these methods based on measurements of freezing-point and solubility of the racemic modification and its mixtures with its *d*- or *l*-form are due to Roozeboom and Bruni.[1] The third Biochemical Method, which depends upon the different actions of the optically active and opposite forms on micro- and higher-organisms, has been devised by one of us.[2]

We have employed Roozeboom's freezing-point (melting-point) method in this investigation. A melting-point-composition-diagram for mixtures of the racemic modification and its *d*- or *l*-form is prepared: a racemic mixture of the *d*- and *l*-forms gives a diagram consisting of two curves with a minimum of temperature, the eutectic point (Type I); the racemic compound gives a diagram consisting of three curves with two minima (eutectic points) and a maximum of temperature (Type II); and the solid solution (mixed crystal) of the *d*- and *l*-isomers will give a single continuous curve joining the melting-points of the optically active and opposite forms

(Type III). In the present investigation we have not come across an example of Type III.

The nature of the middle branch (Type II) often indicates the degree of stability of the compound; if the compound is sufficiently stable, the middle branch forms the greater part of the whole curve and rises and falls abruptly. When the compound is extremely unstable, the middle branch of the curve is smaller and is much flatter in appearance. We have applied these considerations in indicating the degree of stability of the racemic forms.

Experimental

The *dextro-*, *lævo-* and *racemic*-forms of the substances were prepared by methods already described.[3] The melting-point determinations were carried out by preparing an intimate mixture of accurately weighed quantities of the racemic modification and its *d-* or *l*-form and determining the melting-point of the mixture by the capillary-tube method. The melting-points (in ° C.) are given in Tables I–VIII.

Discussion

3-*Nitro*-p-*toluidinomethylenecamphor*.—The melting-point determinations are given in Table I. The melting-point-composition-diagram (Fig. 1) consists of two symmetrical curves with a eutectic point. This shows that the racemic modification is a true *dl*-mixture and conforms to Type I mentioned above.

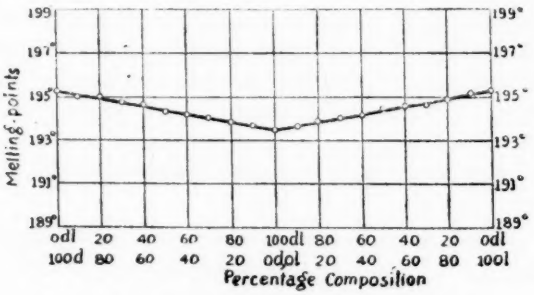

Fig. 1. 3-Nitro-*p*-toluidinomethylenecamphors

5-*Iodo*-o-*toluidinomethylenecamphor*.—The melting-point determinations are given in Table II. The melting-point-composition-diagram (Fig. 2) consists of three curves with two eutectic points. Therefore, the racemic modification is a true *dl*-compound and conforms to Type II mentioned above. It is very stable, and the range of stability is very large as the middle branch is very steep and occupies almost the whole of the diagram.

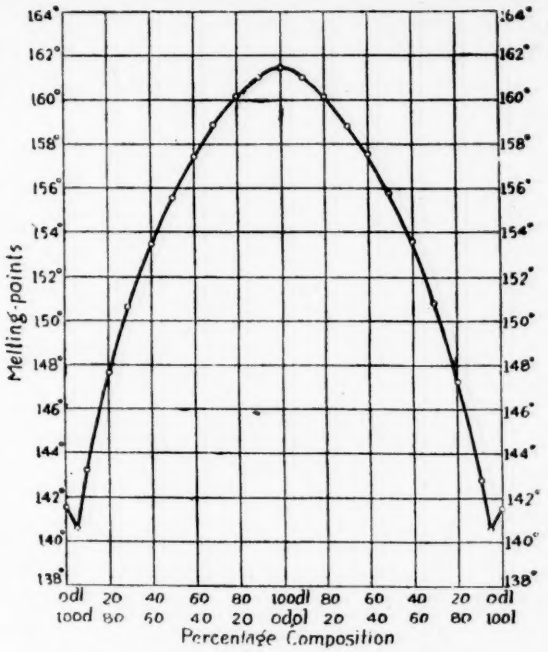

FIG. 2. 5-Iodo-*o*-toluidinomethylenecamphors

4-*Nitro*-o-*toluidinomethylenecamphor*.—The melting-point determinations are given in Table III. The melting-point-composition-diagram (Fig. 3) shows that the racemic modification is a true *dl*-compound (Type II). The shape of the middle branch indicates that it is fairly stable and that the range of stability is fairly large.

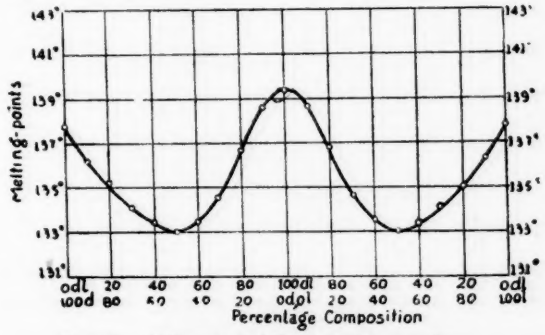

FIG. 3. 4-Nitro-*o*-toluidinomethylenecamphors

Oxymethylenecamphor.—The melting-point determinations are given in Table IV. The melting-point-composition-diagram (Fig. 4) shows that the racemic modification is a true *dl*-compound (Type II). It is stable but the range of stability is small.

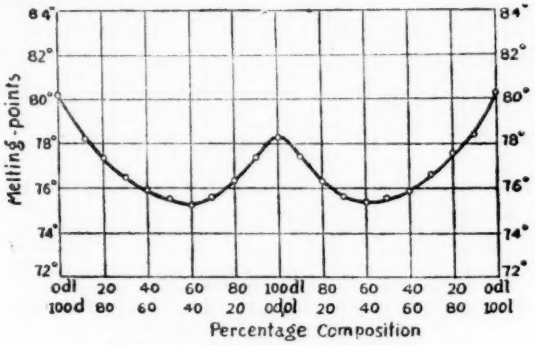

FIG. 4. Oxymethylenecamphors

2-Nitro-p-*toluidinomethylenecamphor.*—The melting-point determinations are given in Table V. The melting-point-composition-diagram (Fig. 5) shows that the racemic modification is a true *dl*-compound (Type II). It is stable but the range of stability is small as is clear from the shape of the middle branch of the diagram.

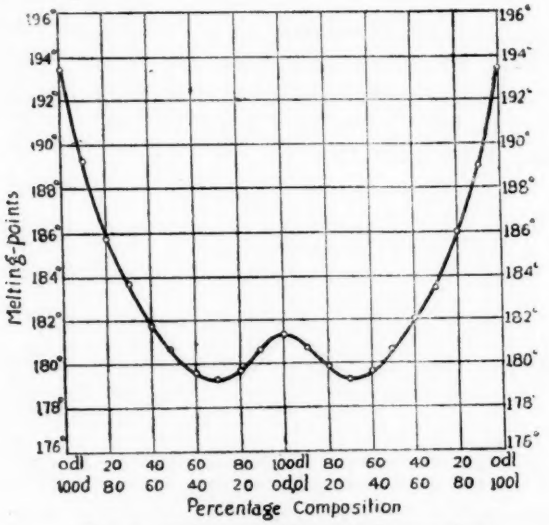

FIG. 5. 2-Nitro-*p*-toluidinomethylenecamphors

3-*Nitro*-4-*chloroanilinomethylenecamphor*.—The melting-point determinations are given in Table VI. The melting-point-composition-diagram (Fig. 6) shows that the racemic modification is a true *dl*-compound (Type II). It is much less stable as the middle curve is flatter in appearance.

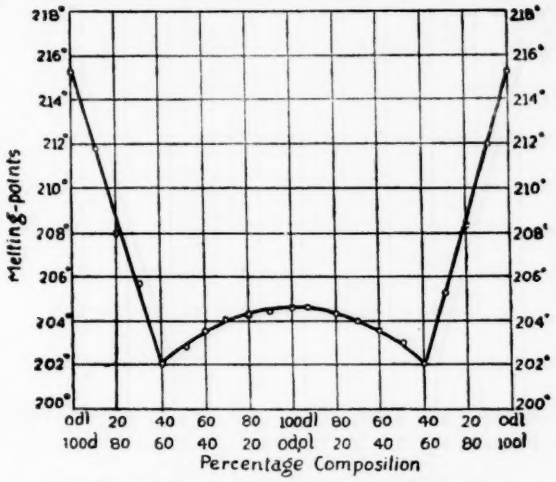

FIG. 6. 3-Nitro-4-chloroanilinomethylenecamphors

2: 5-*Dichloroanilinomethylenecamphor*.—The melting-point determinations are given in Table VII. The melting-point-composition-diagram (Fig. 7) shows that the racemic modification is a true *dl*-compound (Type II) of low stability and that the range of stability is small.

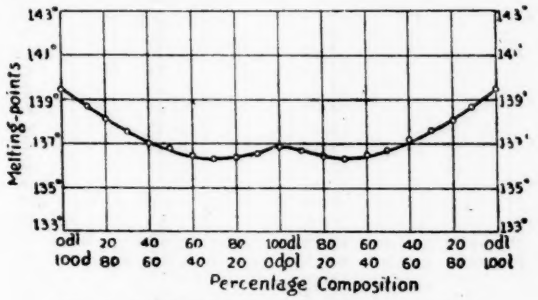

FIG. 7. 2 : 5-Dichloroanilinomethylenecamphors

4-*Chloro*-o-*toluidinomethylenecamphor*.—The melting-point determinations are given in Table VIII. The melting-point-composition-diagram (Fig. 8) shows that the racemic modification is a true *dl*-compound (Type II)

of little stability. The range of stability is very small as indicated by the flat nature of the middle curve.

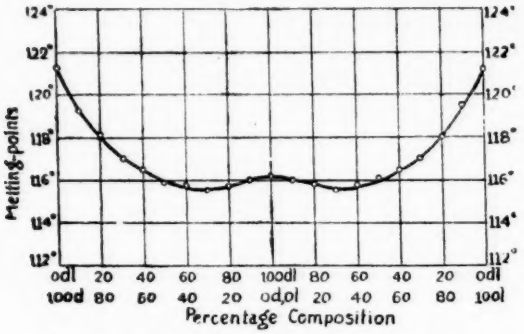

FIG. 8. 4-Chloro-*o*-toluidinomethylenecamphors

TABLE I

3-Nitro-p-*toluidinomethylene-camphors*

Mixed melting-points of the racemic modification with its *d*- or *l*-form.

Wt. % of the racemic modification	Wt. % of the *d*- or *l*-form	Melting-point of the mixture
100	0*d*	193·4°
90	10	193·6
80	20	193·8
70	30	194·0
60	40	194·2
50	50	194·3
40	60	194·6
30	70	194·7
20	80	195·0
10	90	195·0
0	100	195·2
90	10*l*	193·6
80	20	193·8
70	30	194·0
60	40	194·1
50	50	194·4
40	60	194·5
30	70	194·6
20	80	194·8
10	90	195·1
0	100	195·2

TABLE II

5-Iodo-o-*tolnidinomethylene-camphors*

Mixed melting-points of the racemic modification with its *d*- or *l*-form.

Wt. % of the racemic modification	Wt. % of the *d*- or *l*-form	Melting-point of the mixture
100	0*d*	161·4°
90	10	161·0
80	20	160·1
70	30	158·9
60	40	157·4
50	50	155·5
40	60	153·4
30	70	150·6
20	80	147·6
10	90	143·2
5	95	140·6
0	100	141·5
90	10*l*	161·9
80	20	160·0
70	30	158·8
60	40	157·6
50	50	155·8
40	60	153·6
30	70	150·8
20	80	147·2
10	90	142·8
5	95	140·6
0	100	141·5

TABLE III

4-Nitro-o-toluidinomethylenecamphors

Mixed melting-points of the racemic modification with its *d*- or *l*-form.

Wt. % of the racemic modification	Wt. % of the *d*- or *l*-form	Melting-point of the mixture
100	0*d*	139·4°
90	10	138·6
80	20	136·6
70	30	134·5
60	40	133·4
50	50	133·0
40	60	133·4
30	70	134·0
20	80	135·2
10	90	136·2
0	100	137·8
90	10*l*	138·6
80	20	136·8
70	30	134·6
60	40	133·5
50	50	133·0
40	60	133·4
30	70	134·1
20	80	135·0
10	90	136·3
0	100	137·8

TABLE IV

Oxymethylenecamphors

Mixed melting-points of the recemic modification with its *d*- or *l*-form.

Wt. % of the racemic modification	Wt. % of the *d*- or *l*-form	Melting-point of the mixture
100	0*d*	78·2°
90	10	77·3
80	20	76·3
70	30	75·6
60	40	75·3
50	50	75·6
40	60	75·9
30	70	76·4
20	80	77·3
10	90	78·2
0	100	80·2
90	10*l*	77·3
80	20	76·3
70	30	75·5
60	40	75·3
50	50	75·5
40	60	75·9
30	70	76·5
20	80	77·5
10	90	78·3
0	100	80·2

TABLE V

2-Nitro-p-toluidinomethylenecamphors

Mixed melting-points of the recemic modification with its *d*- or *l*-form.

Wt. % of the racemic modification	Wt. % of the *d*- or *l*-form	Melting-point of the mixture
100	0*d*	181·3°
90	10	180·6
80	20	179·7
70	30	179·2
60	40	179·7
50	50	180·6
40	60	181·8
30	70	183·7
20	80	185·8
10	90	189·2
0	100	193·4
90	10*l*	180·6
80	20	179·9
70	30	179·2
60	40	179·6
50	50	180·6
40	60	182·0
30	70	183·4
20	80	186·0
10	90	189·0
0	100	193·4

TABLE VI

3-Nitro-4-chloroanilinomethylenecamphors

Mixed melting-points of the racemic modification with its *d*- or *l*-form.

Wt. % of the racemic modification	Wt. % of the *d*- or *l*-form	Melting-point of the mixture
100	0*d*	204·5°
90	10	204·4
80	20	204·2
70	30	204·0
60	40	203·4
50	50	202·7
40	60	202·0
30	70	205·6
20	80	208·0
10	90	211·8
0	100	215·2
90	10*l*	204·4
80	20	204·2
70	30	203·9
60	40	203·5
50	50	202·9
40	60	202·0
30	70	205·2
20	80	208·4
10	90	212·0
0	100	215·2

TABLE VII

2 : 5-*Dichloroanilinomethylene-camphors*

Mixed melting-points of the racemic modification with its *d*- or *l*-form.

Wt. % of the racemic modification	Wt. % of the *d*- or *l*-form	Melting-point of the mixture
100	0*d*	136·8°
90	10	136·6
80	20	136·4
70	30	136·2
60	40	136·4
50	50	136·7
40	60	137·0
30	70	137·5
20	80	138·1
10	90	138·7
0	100	139·4
90	10*l*	136·6
80	20	136·3
70	30	136·2
60	40	136·4
50	50	136·6
40	60	137·1
30	70	137·5
20	80	138·0
10	90	138·7
0	100	139·4

TABLE VIII

4-*Chloro*-o-*toluidinomethylene-camphors*

Mixed melting-points of the racemic modification with its *d*- or *l*-form.

Wt. % of the racemic modification	Wt. % of the *d*- or *l*-form	Melting-point of the mixture
100	0*d*	116·2°
90	10	116·0
80	20	115·7
70	30	115·5
60	40	115·7
50	50	115·9
40	60	116·4
30	70	117·0
20	80	118·1
10	90	119·2
0	100	121·2
90	10*l*	116·0
80	20	115·8
70	30	115·5
60	40	115·7
50	50	116·1
40	60	116·5
30	70	117·1
20	80	118·0
10	90	119·5
0	100	121·2

SUMMARY

The racemic modification of 3-nitro-*p*-toluidinomethylenecamphor is a true *dl*-mixture whereas the racemic modifications of 5-iodo-*o*-toluidino-, 4-nitro-*o*-toluidino-, oxy-, 2-nitro-*p*-toluidino-, 3-nitro-4-chloroanilino-, 2 : 5-dichloroanilino- and 4-chloro-*o*-toluidino-methylenecamphors are all true *dl*-compounds.

The stability of the racemic forms is also discussed.

We wish to thank the University of Allahabad, where this work was done, for the provision of research facilities.

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CONSTITUTION OF GOSSYPIN—PART II

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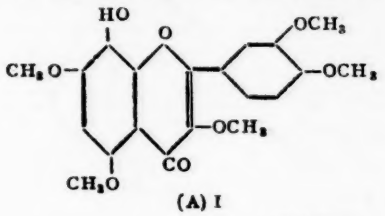
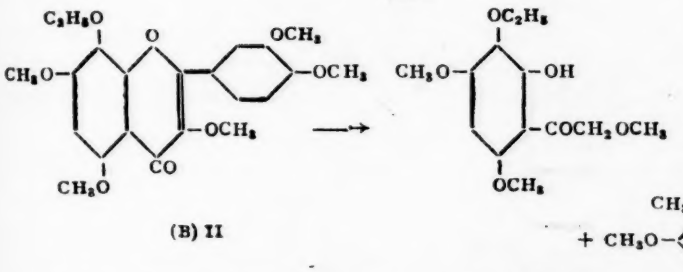
Received March 10, 1947

In Part I[1] experiments were described which led to the conclusion that gossypin is the 8-monoglucoside of gossypetin. After complete methylation and subsequent hydrolysis a pentamethyl gossypetin (A) was obtained whose constitution as an 8-hydroxy compound (I) was arrived at by a process of elimination of all other possibilities. Since this type of glucoside is extraordinary and unusual, further study of the degradation product (A) was considered to be necessary to make sure of the position.



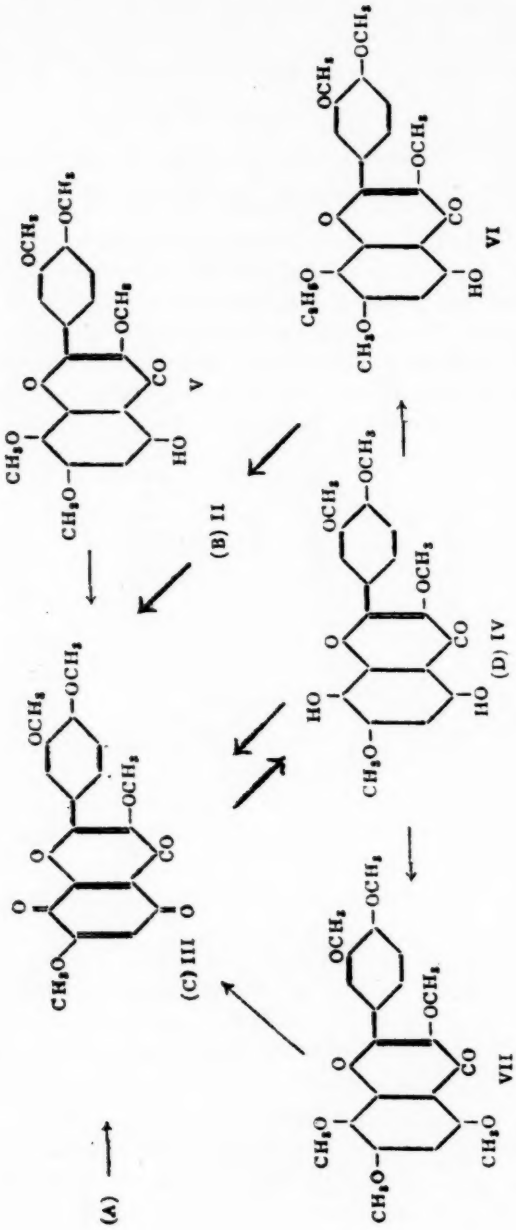
(A) I



(B) II

It has already been mentioned that alkali fission of compound (A) does not proceed well. Though veratric acid could be obtained as a product, the ketonic part could not be isolated. However, the ethyl ether (B) is now found to undergo smooth fission yielding besides veratric acid a ketone whose analysis indicates that it has an ethoxyl group in it.

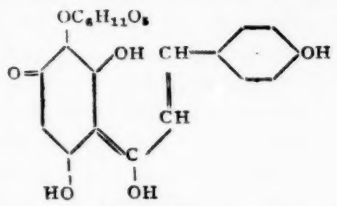
The most interesting results have been obtained by the oxidation of the pentamethyl gossypetin (A) with nitric acid. The reaction takes place readily and a quinone (C) is produced which could be smoothly reduced to a


(A)
(B) II
(C) III
(D) IV
V
VI
VII

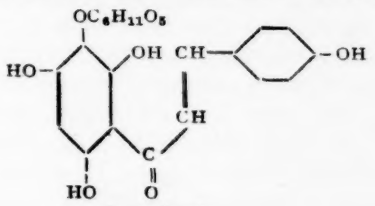
quinol (D). The same quinone and quinol are formed under the same conditions from pentamethyl gossypetin having a hydroxyl group in the 5-position (V) which could be readily made by the partial methylation of gossypetin. Consequently the quinone (C) and quinol (D) should be represented by formulæ (III) and (IV). This difinitely supports the 8-hydroxy constitution (I) for pentamethyl gossypetin (A). Confirmation of this has again been obtained by the partial ethylation of the quinol which should be expected to take place in the 8-position (VI). Subsequent methylation yields a pentamethyl-monoethyl ether whose constitution should be represented by formula (II). This substance is found to be identical with the ethyl ether (B) obtained from gossypin.

That no change other than what has been represented above takes place has been proved by the complete methylation of the quinol whereby hexamethyl gossypetin (VII) is obtained, In continuation of the above oxidation experiments it has been found that even this hexamethyl ether could be oxidised to the above mentioned quinone under almost the same conditions. In this respect the ethyl ether (B) also behaves similarly.

Though among the anthoxanthins an 8-glycoside structure has been established for the first time in gossypin, glycosidation of the 8-position need not be considered as unexpected if the related phenomenon of partial methylation is taken into consideration. The possibility was indicated by the existence of wogonin[2] which is a monomethyl ether of 5:7:8-trihydroxy-flavone having the methoxyl in the 8-position. A constitution somewhat analogous to gossypin has been suggested for carthamin[3], the glycosidic pigment of safflower; but there seems to be no definite evidence in support.



Carthamin



Iso-carthamin

EXPERIMENTAL

Ethylation of pentamethyl gossypetin (A) obtained from gossypin; Preparation of the ethyl ether (B):—

A solution of the substance (A) (1 g.) in anhydrous acetone (50 c.c.) was treated with ethyl iodide (2 c.c.) and potassium carbonate (10 g.). After refluxing for 10 hours the solvent was completely removed and the

residue treated with water. The precipitated ethyl ether was filtered, washed and purified by crystallising twice from alcohol from which it separated in the form of colourless elongated rectangular plates melting at 142–43°. Yield 0·9 g. (Found: C, 61·1; H, 5·9; $C_{22}H_{24}O_8$, H_2O requires C, 60·8; H, 5·9%.). It was not soluble in aqueous alkali and did not give any colour with ferric chloride.

Alkali fission of the ethyl ether (B):—

The ethyl ether (1 g.) was refluxed for 6 hours with absolute alcoholic potash (30 c.c. of 10% solution). The solvent was then completely removed, the residue dissolved in water and the clear brown solution acidified with hydrochloric acid. It was repeatedly extracted with ether and the ether extract shaken with aqueous sodium bicarbonate twice. After washing with water the ether extract was evaporated when the ketonic product was left behind in a crystalline condition. It crystallised from dilute alcohol as almost colourless needles melting at 128–29°. (Found: C, 57·3; H, 6·3; $C_{13}H_{18}O_6$ requires C, 57·7; H, 6·6%). It was soluble in aqueous sodium hydroxide to give a pale yellow solution. In alcoholic solution it gave a reddish brown colour with ferric chloride.

The bicarbonate extract, on acidification, deposited a crystalline solid which was filtered, washed and crystallised twice from hot water. It melted at 180–82° and the mixed melting point with veratric acid was not depressed.

Gossypetone tetramethyl ether (*III, C*):—

(*a*) *From gossypetin pentamethyl ether* (*V*).—Gossypetin pentamethyl ether (0·5 g.) was treated with nitric acid (10 c.c., d. 1·25) with stirring while cooling the reaction mixture in ice-water. The solid rapidly dissolved in the acid forming an intense red solution which very quickly deposited a reddish brown solid. After keeping the mixture well stirred at 15–20° for 15 minutes it was filtered and the residue washed free from nitric acid. It was then crystallised from glacial acetic acid from which it came out as brick-red flat needles melting at 245–47°. (Found: C, 58·6; H, 5·0; $C_{19}H_{16}O_8$, H_2O requires C, 58·5; H. 4·6%.). Yield, 0·4 g. It was very sparingly soluble in alcohol and moderately in glacial acetic acid. In aqueous sodium hydroxide it dissolved to a bluish-violet solution.

(*b*) *From the pentamethyl ether* (*A*).—The above reaction was carried out with this pentamethyl ether (0·5 g.). The reaction was very rapid and the quinone separated out in good yield. It was filtered and washed well. It crystallised from glacial acetic acid in the form of brick-red flat needles

melting at 245–47° alone or when admixed with the quinone described above. Its properties were also identical with those of the above.

(*c*) *From gossypetin hexamethyl ether* (*VII*).—Gossypetin hexamethyl ether (0·5 g.) was treated with nitric acid (15 c.c., d. 1·25) with stirring. The solid slowly dissolved producing first a yellow solution which gradually deepened to orange and finally to deep red with the separation of a reddish-brown solid. After allowing the mixture to stand for 30 minutes at a temperature of 15–20° the solid was filtered off; washed first with nitric acid (d. 1·25) and finally with water. It was purified by crystallisation from glacial acetic acid when it separated out in the form of brick-red flat needles melting at 245–47°. It was identical with the quinone prepared by the above two methods.

(*d*) *From pentamethyl-mono-ethyl ether of gossypetin* (*II*, B).—The reaction with this compound proceeded just as in the case of the hexamethyl gossypetin and the quinone was also the same.

3:7:3′:4′-*O-Tetramethyl gossypetin* (*IV*, *D*):—

Gossypetone tetramethyl ether (prepared from each one of the above methods) (0·5 g.) was suspended in glacial acetic acid (2–3 c.c.) and treated with a pinch of sodium sulphite. On heating for a few seconds the deep red colour of the solid as well as the solution turned bright yellow. After stirring vigorously for 5 minutes the mixture was diluted with water and the yellow solid filtered and washed with water. It crystallised from glacial acetic acid in the form of golden yellow elongated thick rectangular prisms melting at 251–53°. (Found: C, 60·6; H, 4·6; $C_{19}H_{18}O_8$ requires C, 61·0; H, 4·8%.). It was sparingly soluble in alcohol and moderately in glacial acetic acid. In alcoholic solution it gave with ferric chloride a transient green colour which quickly changed to brown. When treated with a small quantity of *p*-benzoquinone in absolute alcoholic solution it was slowly oxidised to gossypetone tetramethyl ether which separated out as a red solid. In aqueous sodium carbonate it was insoluble but in sodium hydroxide it readily dissolved to a deep red solution which changed rapidly on shaking with air to bluish violet.

The dihydroxy compound (0·2 g.) was acetylated by boiling with acetic anhydride (1 c.c.) and a few drops of pyridine for one hour. On adding ether to the cooled reaction mixture the acetate crystallised out. It was filtered and washed with a little more ether. It crystallised from absolute alcohol in the form of colourless long matted needles melting at 227–28°. (Found: C, 60·6; H, 5·1; $C_{23}H_{22}O_{10}$ requires C, 60·3; H, 4·8%.) It

was very sparingly soluble in alcohol but was easily soluble in chloroform. It was not soluble in cold aqueous alkali and did not give any colour with ferric chloride.

The dihydroxy compound (0·2 g.) was methylated using dimethyl sulphate (0·5 c.c.) and anhydrous potassium carbonate (5·0 g.) in acetone medium (20 c.c.). After refluxing for 6 hours the solvent was removed, the residue treated with water and the precipitated solid filtered and washed. It was crystallised from alcohol from which it separated out as colourless narrow rectangular plates melting at 170–72° alone or when admixed with the hexamethyl ether of gossypetin.

8-*Ethoxy*-5-*hydroxy*-3 : 7 : 3′ : 4′-*tetramethoxy-flavone* (VI):—

A solution of the dihydroxy compound (IV) (0·5 g.) in anhydrous acetone (50 c.c.) was treated with ethyl iodide (0·12 c.c.) and potassium carbonate (5·0 g.) and the mixture refluxed for 6 hours. The solvent was then removed, the residue treated with water and the yellow solid that separated out was filtered and washed with water. After crystallisation from alcohol it was obtained in a crystalline condition but melted indefinitely between 145–55° showing admixture with the fully ethylated compound. It was therefore dissolved in absolute alcohol (10 c.c.) treated with just enough absolute alcoholic potash and the deep orange solution was evaporated quickly on a water-bath to dryness. The orange red crystalline solid thus obtained was washed repeatedly with boiling benzene and filtered. The residue was suspended in water, treated with dilute hydrochloric acid, heated for a few minutes on a water bath and filtered. It crystallised from absolute alcohol in the form of glistening lemon-yellow elongated rectangular prisms melting at 155–56°. (Found: C, 62·9; H, 5·8; $C_{21}H_{22}O_8$ requires C, 62·7; H, 5·5%.) It was very sparingly soluble in aqueous sodium hydroxide and in alcoholic solution gave an intense green colouration with ferric chloride. Yield, 0·35 g.

8-*Ethoxy*-3 : 5 : 7 : 3′ : 4′-*Pentamethoxy-flavone* (*II*):—

A solution of the above 5-hydroxy compound (0·2 g.) in dry acetone (20 c.c.) was refluxed with dimethyl sulphate (0·5 c.c.) and potassium carbonate (5·0 g.) for 6 hours. The solvent was distilled off, the residue treated with water and the white solid that separated out was filtered and purified by crystallisation from alcohol whereby it came out as colourless elongated rectangular plates melting at 142–43° alone or in admixture with the ethoxy-pentamethoxy-flavone (B) derived from gossypin.

Summary

The constitution of gossypin as the 8-monoglucoside of gossypetin is confirmed by a detailed study of the pentamethoxy monohydroxy-flavone obtained by the complete methylation and subsequent hydrolysis of the glucoside. It is different from gossypetin-pentamethyl ether containing a free hydroxyl group in the 5-position but both give on oxidation the same quinone which is transformed into a quinol. Further its ethyl ether is shown to have the ethoxyl in the 8-position by unambiguous synthesis.

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SAMARSKITE FROM NELLORE DISTRICT

Part I. Uranium and Earth Acid Contents

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Introduction

Samarskite is a primary uranium mineral and is of rare occurrence. In India it has been reported from a few localities and in all cases, sporadically. The occurrence of this rare mineral in the mica-pegmatites of Nellore was reported by Tipper.[1, 2, 3]

The identification of this mineral by Tipper was apparently based only on its megascopic characters and qualitative analysis carried out by Blyth. Yajnik and Kohli[4] carried out determinations of radioactivity of some Indian minerals including samarskite. Samarskite and allied minerals offer analytical problems quite different from and considerably more difficult than those met with in the analysis of silicates. These minerals contain columbium and tantalum, several metals of the rare earths, thorium, titanium, zirconium, vanadium, uranium and some of the more common elements. Perhaps this accounts for the paucity of analytical data on the Nellore samples.

There are several interesting problems connected with samarskite. Euxenite is an alteration product and Smith[5] found that in North Carolina these two occur together. A closely allied mineral Hatchettolite has also been described by Dana (1876) and Smith (*loc. cit.*). No investigations appear to have been carried out in the Nellore area on the possible occurrence of these minerals. Further, samarskite contains several elements of the rare earth group and their identification and quantitative separation is of considerable interest. Finally since this mineral is primary, a determination of the uranium-thorium and lead ratio would enable a calculation of the age of the rock.[6]

In a previous note[7] the present authors pointed out that although accurate calculation of radium content of uranium minerals requires radioactivity measurements, an approximate figure could be obtained by calculation from the uranium content of an unaltered mineral by using the formula of Roberts,[8] *viz.*, % uranium $\times$ 3·4 = mgm. of radium per ton. With the available data for the uranium-bearing silicate minerals, allanite and zircon (cyrtolite) these calculations were made and results reported

(*loc. cit.*) but as no analytical data was available on the Nellore samarskite, this could not be done for this mineral.

The object of the present paper is to report on the results obtained in our preliminary investigations on Nellore samarskites.

Samples

The samples of samarskite were secured from the Kodanda Rama mine in Nellore District. The mine is situated in a pegmatite vein having a strike of roughly N.N.W.-S.S.E. and almost perpendicular dip. The pegmatite is composed of large felspar and quartz crystals with books of mica. About sixty samples were collected from this mine and out of these, six representative samples were chosen for detailed investigation. The radioactivity of the samples was established by the photographic method.[7]

Megascopic Characters

The megascopic characters are given below in the table:—

Sample No.	Sp. Gr.	Hardness	Colour	Lustre	Streak	Cleavage	Fracture	Remarks
1	5·567	5	Dark steel grey	Vitreous	Dark-brown	Nil	Conchoidal	Intergrown with Columbite-Tantalite
2	5·570	6	Velvet black	Resinous	Brown	do	do	
3	5·677	6	do	do	do	do	do	
4	5·634	6	do	do	Reddish brown	do	do	
5	5·776	6	Black	Splendent	do	do	Uneven	
6	5·628	6	Velvet black	do	Dark-brown	do	do	Separated from Columbite-Tantalite

The above properties agree closely with those given by Dana[9] for samarskite. However, it should be noted that sample No. 1 is actually a coarse intergrowth of two minerals which are distinctly visible to the naked eye. Auto-radiographic evidence for this fact s reproduced below.

The auto-radiograph was taken by placing a polished surface in close contact with a panchromatic photographic plate covered with black paper and leaving them together in a dark cabinet for one week and developing the plate afterwards.

Fig. 1 is an actual photograph of the polished specimen and Fig. 2 is the corresponding auto-radiograph. Sample No. 6 was obtained from a specimen of samarskite intergrown with columbite-tantalite from which

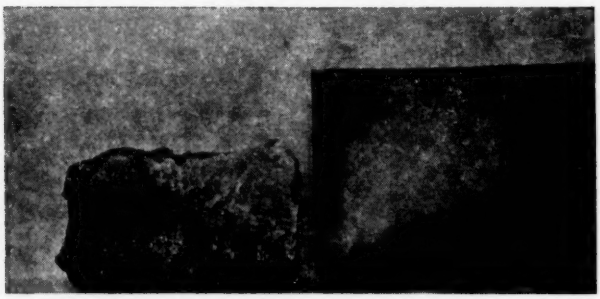

FIG. 1 FIG. 2

the non-samarskite portion was carefully separated. The columbite-tantalite minerals are closely associated with samarskite in this locality and it is not therefore surprising that the second mineral has been definitely identified as a columbite-tantalite by chemical analyses. It may be mentioned in passing that though there are small, normally insignificant, differences in properties among the samples, megascopically all of them appear to be samarskite.

CHEMICAL ANALYSIS

The samples were analysed primarily for their uranium content by the method described by Schoeller and Powell.[10] Uranium occurs in samarskite in both the quadrivalent and hexavalent states but their differentiation is not possible by this method of analysis. Hence the results are being reported in terms of UO_3 in the table below. Our results showed a greater degree of variation of UO_3 (5·6 to 10·5%) than those recorded by Swallow, Smith and Allen[9] for samarskite samples from N. Carolina, *viz.*, 10·9 to 12·5% UO_3. For comparison the mixed earth acid contents were determined approximately quantitatively by igniting and weighing the insoluble residue obtained by extracting the pyrosulphate melt with dilute hydrochloric acid.

Sample No.	UO_3%	Nb_2O_5 plus Ta_2O_5
1	4·2	69·7
2	10·5	54·3
3	6·1	59·2
4	8·7	54·0
5	5·6	58·4
6	8·4	53·4

This residue consists mainly of columbium and tantalum pentoxides contaminated by very small amounts of titania, stannic oxide, tungstic oxide, etc. The percentages of these minor constituents do not add to more than

two units. It is interesting to note that even in these values, there is divergence from the figures given by the authors referred to[9] (average value 55·3%). The divergence with the first sample is especially high but this can be readily explained as it is an intergrowth of two minerals, the other part being a columbite-tantalite. Sample 5 shows some difference in colour, lustre and fracture from pure samarskite but Sample 3 is a typical sample of this mineral. Megascopically these samples do not show any dissemination of another mineral.

The authors wish to express their grateful thanks to Prof. C. Mahadevan for his kind interest in the work.

Summary

1. Sixty samples of samarskite were collected from a mica pegmatite vein in Nellore district, S. India.

2. The physical and chemical properties of six representative samples from this collection were studied.

3. Numbers 1 and 6 of the selected samples of samarskite were intergrown with Columbite-Tantalite.

4. The specific gravity of these six specimens varies from 5·567 to 5·776. The hardness is between 5 and 6. The colour varies from dark steel grey to velvet-black and the streak is generally brown to dark-brown. They all break with conchoidal fracture.

5. Specimen No. 1 which is an intergrowth of samarskite with Columbite-Tantalite was polished and placed in contact with a panchromatic photographic plate. Only the samarskite portion affected the photographic plate.

6. The chemical analysis of samarskite shows a variation in UO_3 percentage from 4·2 to 10·5% and the $Nb_2O_5 + Ta_2O_5$ from 53·4 to 69·7%. Attention is drawn to the fact that the UO_3 percentages of samarskite from the Nellore area differ from those of North Carolina.

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DIELECTRIC CONSTANTS OF CRYSTALS

I. Different Types of Quartz

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1. Introduction

Various authors determined the dielectric constants of colourless quartz. Results reported are at variance with each other to an appreciable extent. Cady,[1] agreeing with Sosman,[2] gives the most probable values of $K_{\perp}$ ($\perp^{r}$ to the optic axis) as 4·5 and $K_{\parallel}$ ($\parallel^{el}$ to the optic axis) as 4·6 for quartz.

In the case of colourless quartz, data are available not only in respect of the dielectric constants but also in respect of their dependence on temperature, frequency and so on. No work appears to have been done on amethyst, smoky quartz or other coloured types. There are different opinions as to the origin of the colour in each case. One view[3] is that amethyst owes its colour to a compound of ferric iron which is stable up to 260° C. Other views have been expressed in the literature. Similarly, the cause of colour in smoky quartz is taken as the presence of an inorganic pigment by some and as free silicon liberated by radioactive radiations by some others.[3] The latter view has gained much strength in view of the facts that smoky quartz occurs generally in the neighbourhood of radioactive ores, and that in general it is possible under X-radiation to convert colourless quartz into smoky quartz. This problem of the origin of colour of smoky quartz and amethyst has not yet been fully cleared up and in the hope that their dielectric behaviour may throw some light on the subject, the author has undertaken a study of the same.

2. Experimental

The usual method for determining the dielectric constant of a solid body is to take it in the form of a plate and find the change in capacity it produces when placed between the plates of a parallel plate condenser. The latter forms part of the tank circuit of an oscillator in a heterodyne unit. A mixture method is also in vogue for solids and is widely used in the case of powders. The dielectric constants of a number of mixtures of two suitable liquids are found when they are pure and when they contain a

particular amount of the solid. The values in the latter case will be different from the former. By taking suitable liquid mixtures of dielectric constants above and below that of the solid and drawing a graph between the original values of the mixtures and the change produced by the solid, the dielectric constant of the solid, which corresponds to the value of mixture having no change on the introduction of solid, can be obtained. In this investigation, the mixture method is employed in a modified form. Instead of determining the dielectric constants of several liquid mixtures with and without the solid inside, a liquid mixture is adjusted to have the same dielectric constant as the solid by varying the proportions of the constituents.

A liquid cell with two parallel plates, the distance between which can be suitably adjusted, is connected to the tank circuit of one of the oscillators of a heterodyne unit. Another small variable condenser consisting of two parallel plates, one of which can be moved from a distance by an insulating handle, is also connected parallel to the above. The plate distance in the liquid cell is adjusted to be a little more than the thickness of the crystal section under study. The crystal is fixed to a glass fibre suspension with a small drop of shellac. The suspension head can be moved up or down by means of a pulley arrangement. A mixture of benzene and nitrobenzene is poured in the liquid cell. The oscillators are adjusted for the beat note of a low frequency and from a distant control, the crystal is moved in between the plates of the liquid cell. By the change in the beat note, even a very small difference in the dielectric constants of the liquid mixture and the crystal plate can be recognized. The liquid mixture proportions are thus suitably adjusted such that it has the same dielectric constant as the crystal plate. The dielectric constant of the liquid mixture so arrived at is determined using a special liquid cell supplied by Kipp & Zonen, Holland. In this determination, the leads correction, obtained by using double distilled benzene, is taken into account. Measurements repeated on different occasions show that values which differ from each other by less than 1% are obtained.

The liquid level is kept more than one centimetre above the plates in the liquid cell used for containing the crystal. When the final adjustment is made, it is seen that the crystal plate is completely immersed in the liquid. The immersion does not produce any change in the capacity due to changes in the liquid level because the liquid level is already well above the condenser plates.

Two Y cut and two Z cut plates of colourless quartz, four specimens of amethyst with different shades of colour cut into thin plates perpendicular

to the Z axis and two plates of smoky quartz cut from a lump without any definite orientation have been studied in this investigation.

The amethyst and smoky quartz plates have been heated in the air oven at about 400° C. for four to five hours and then transferred to a desiccator. As the amethyst bits developed cracks on heating, it was found necessary to keep them free from moisture. On heating, the smoky quartz plates

TABLE I

Specimen No.	Orientation	Dielectric constant	
		Author	From Cady[1]
1	Y cut	4·40	4·5
2	,,	4·50	
3	Z cut	4·60	
4	,,	4·50	4·6

TABLE II

Specimen No.	Description of the Section	Dielectric constant	
		Before heating	After heating
1	Smoky quartz. Light smoky brown in colour. Uniform throughout. After heating colour is completely lost, leaving a yellowish tinge all through.	4·50	4·55
2	Smoky quartz. This also has a quite uniform smoky brown colour of slightly less intensity than that of No. 1. After heating colour has entirely vanished with the same yellowish tinge as for No. 1 remaining.	4·50	4·50
3	Amethyst. Violet colour all through with three intense streaks resembling sectors in shape. After heating, background colour is completely lost, but the streaks are still present with much less intensity.	5·40 half portion 5·30 other half	5·40
4	Light violet colour in the back ground with two patches of less intensity than those of No. 3. After heating, the patches only stand with less intensity.	5·15	5·10
5	It has got the usual lightly violet background colour two patches of different intensities, both of them being less intense than in No. 4. After heating, the background colour and the less intense patch have almost vanished. But the other patch still remains weak.	4·90	4·85
6	Throughout it possesses very light and uniform violet colouration with no patches. After heating colour is completely gone, leaving a dull yellow tinge.	4·90	5·00

lost the colour completely within half an hour. One amethyst bit lost the colour completely on heating for four hours. Though the others lost it to a great extent, some light patches of colour remained here and there. The dielectric constants of all the above sections have been redetermined after heat treatment.

3. Results

In determining the dielectric constant of the neutralising liquid mixture, the value for benzene was taken to be 2·27 at the room temperature 26° C. for finding the leads correction for the liquid cell. The determinations were made at frequencies ranging between one and two mega-cycles per second. The results obtained with colourless quartz plates are given in Table I.

The results obtained with amethyst and smoky quartz sections are given in Table II.

4. Discussion of Results

There is a definite difference between the dielectric constants of the two specimens of quartz studied as Y cut plates. The same applies to the pair of Z cut plates. A repeated determination consecutively of the values of the above specimens gave the differences consistently. This shows beyond doubt that the dielectric constants of quartz may vary slightly from specimen to specimen.

The dielectric constant of a single plate of amethyst is not uniform throughout. By the changes in the beat note, it is found that different portions of the plate have slightly different values. In the case of specimen No. 3 the values for the two halves of the plate taken are given. For some other plates also there are slight variations but the values for the central portions only are given. For the colourless quartz and smoky quartz the values are uniform throughout the plate.

There are slight differences in the values of the decolourised specimens when compared with the corresponding coloured specimens. Nothing definite can, however, be said about them. Some of these differences are within experimental errors and some may be due to traces of moisture absorbed by the bits in handling.

It is interesting to note that the dielectric constants of smoky quartz agree with those of colourless quartz whereas the constants of amethyst are definitely higher. The colour of the smoky quartz is generally believed to be due to irradiation by radioactive substances and not due to metallic content,[3, 4] The fact that the dielectric constant of smoky quartz is not

different from that of colourless quartz is significant in this respect, because as appreciable metallic content may be expected to change the dielectric constant.

The dielectric constant of amethyst is definitely higher than that of normal quartz and also it remains the same even though the specimen is decolourised. In view of the appreciable iron content in amethyst as shown by Holden,[3] this is explicable. As the amethyst plates are not uniformly coloured with gradations in intensity, a regular relation between intensity of colour and dielectric constant could not be obtained. Though specimens No. 5 and No. 6 are of different intensities, there is no difference in their dielectric constants. But Nos. 3 and 4 whose colour intensity is higher than that of No. 5 or No. 6 have higher dielectric constants. Thus in general amethysts of greater colour intensity appear to have higher dielectric constants.

5. Summary

The dielectric constants of colourless quartz, smoky quartz and amethyst are found by a modified liquid mixture method. The constants of different specimens of colourless quartz are slightly different from each other. The smoky quartz has its dielectric constant agreeing with that of colourless quartz. This value remains the same before and after decolourisation by heat treatment. Amethyst specimens have higher dielectric constants than colourless quartz and such values are unchanged by decolourisation.

The author wishes to express his grateful thanks to Prof. S. Bhagavantam under whose guidance the above investigation has been carried out. His thanks are due to Mr.. Bh. Krishnamurty for lending the amethyst and smoky quartz sections prepared by him.

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ELASTIC CONSTANTS OF MAGNETITE, PYRITE AND CHROMITE

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1. Introduction

After the classical work of Voigt, much has not been done on the elastic properties of crystals. This is due to want of a suitable method. Recently Bhagavantam and Bhimasenachar (1944) developed a method which has opened up a new field of research in this direction. This paper deals with the determination of the elastic constants of Magnetite, Pyrite and Chromite by utilising this new method.

2. Magnetite

Magnetite belongs to the isomorphous series of oxide minerals of the Spinel group with the general formula $R_2O_3.RO$. In magnetite both the radicals are iron, one being ferrous and the other ferric. Magnetite crystallises in the holohedral class of the cubic system and the common form is the octahedron. Twinning occurs about the octahedral plane. Cleavage is not distinct but an octahedral parting is often highly developed. The specific gravity of magnetite ranges from 4.96 to 5.40—the average being 5.16. The values for the two specimens investigated by the author are 4.98 and 5.11. The presence of impurities in the mineral is said to account for the variation in specific gravity. F. D. Adams studied its compressibility. He tried the effect of compression upto 43,000 lbs. applied in 17 minutes on a crystal and found that the mineral broke to pieces, and that the fragments had the form of thin plates which separated from the crystal parallel to the octahedral faces. There were no signs of plastic deformation. Bridgemann (1925), L. H. Adams and Madelung and Fuchs (1921) have determined the compressibility of magnetite (Mellor, 1935). Individual constants for the crystal have not so far been determined.

Two well-formed crystals of magnetite, octahedral in form, from the tremolite-magnetite schists at Holenarsipur in Mysore were chosen and used for the study. Plates (100) and (111) were cut from each of the crystals. The natural frequencies of the plates were determined by the ultrasonic wedge method and the elastic constants are deduced therefrom.

The values for the two specimens, denoted by A and B are given below:

	A	B
C_{11}	27·5 × 10^{11} dynes/sq. cm.	27·0 × 10^{11} dynes/sq. cm.
C_{12}	10·4 × 10^{11} ,, ,,	10·8 × 10^{11} ,, ,,
C_{44}	9·55 × 10^{11} ,, ,,	9·87 × 10^{11} ,, ,,

The bulk modulus for each of the above specimens is calculated by evaluating $\frac{C_{11} + 2C_{12}}{3}$ and the values obtained along with those of previous workers are given below (Mellor, 1935):

Worker	Value
Bridgemann ..	16·94 × 10^{11} dynes/sq. cm.
L. H Adams ..	17·8 × 10^{11} ,, ,,
Madelung and Fuchs ..	17·8 to 17·2 × 10^{11} ,,
Author's A ..	16·1 × 10^{11} ,, ,,
Author's B ..	16·2 × 10^{11} ,, ,,

3. Pyrite

The term pyrites is often used to include the two dimorphous varieties of iron sulphide and the mineral pyrrhotite. Here the term pyrite is used to denote only the cubic form of iron disulphide. The most common forms are the cube and the pentagonal dodecahedron. Pyrite sometimes imperfectly cleaves along the planes (100) and (111). The specific gravity ranges from 4.6 to 5.1.

The specimens of pyrite used in the investigations were collected from limestones of Purana age near Macherla in Guntur district. They are studded in certain layers of the limestone flags and show successive stages of alteration to limonite. Plates parallel to the cubic face (100) and at 45° to the same, *viz.*, the dodecahedral (110) were cut from the unaltered crystals and their elastic constants determined. The values obtained for the four specimens studied are given below in units of 10^{11} dynes/sq. cm.

	A	B	C	D
C_{11} ..	36·16	35·85	35·78	37·51
C_{12} ..	−4·44	−5·29	−4·39	−4·85
C_{44} ..	10·84	10·35	10·85	10·14

The results of the chemical analyses of the four specimens are:

	A	B	C	D
Iron ..	44·51	45·19	45·24	44·59
Sulphur ..	51·81	50·77	50·68	50·46
Insolubles ..	3·04	3·32	4·36	4·37
Total ..	99·6	99·28	100·28	99·42

4. Chromite

Chromite belongs to the spinel group of minerals. As is characteristic of that group, it occurs commonly in octahedrons. Very often it occurs as combinations of the octahedron and the dodecahedron. It is a double oxide of ferrous iron and chromium having the formula $FeO.Cr_2O_3$. Its specific gravity is between 4.32 and 4.57. Chromite is found in ultrabasic igneous rocks like peridotites and pyroxenites. It is one of the earliest minerals formed during the solidification of the magma.

The specimen of chromite investigated was collected from near Kondapalle in Kistna district. Here chromite occurs as a segregation product among the ultrabasic rocks of the area. The specimen selected for study was a big crystal of about $1\frac{1}{2}$ to 2 inches along the crystallographic axis. The octahedral faces were well developed.

The values of the constants obtained from the two plates (111) and (100) are $C_{11} = 32.25 \times 10^{11}$ dynes/sq. cm.; $C_{12} = 14.37 \times 10^{11}$ dynes/sq. cm. and $C_{44} = 11.67 \times 10^{11}$ dynes/sq. cm. The bulk modulus comes out as 20.3×10^{11}.

5. Discussion of the Results

The variations in the values of the elastic constants of the two specimens of magnetite are very small. These variations are attributable to the small changes in the chemical composition of the specimens or to the presence of slight impurities, which are to be expected as there is a difference in the densities of the two specimens.

All the four specimens of pyrite investigated exhibit the characteristic negative constant C_{12}. The presence of the negative constant for pyrite was first reported by Voigt and it has since been confirmed by Bhimasenachar using the new wedge method in the cases of specimens from Nepal (of igneous origin) and from Betamcherla (of sedimentary origin). The specimens now worked were chemically analysed to see if the variations show any relationship to the chemical composition. Variation in the individual values

of C_{11}, C_{12} or C_{44} for each of the specimens do not appear to have any definite relationship with the composition.

In the case of garnets worked out by Ramachandra Rao (1945), though there was no regular relation between the individual constants and composition, the bulk modulus varied regularly with the iron content. When a similar correlation is attempted between the bulk modulus and the extra iron content of the four specimens of pyrite, none is found to exist.

6. Summary

Using the ultrasonic wedge method recently developed by Bhagavantam and Bhimasenachar, the elastic constants of two specimens of magnetite from Holenarasipur in Mysore have been determined. The values of the bulk moduli for these have been compared with the values obtained by the previous workers. The elastic constants of four specimens of pyrite from Macherla in Guntur district have been determined. In conformity with earlier reports, C_{12} is found to be negative in these cases. The elastic constants of a specimen of chromite from Kondapalle in Kistna district have also been determined.

This work was carried out in the Geology and Physics Laboratories of the Andhra University. The author's heartfelt thanks are due to Prof. C. Mahadevan, D.Sc., for his direction, to Prof. S. Bhagavantam, Hon. D.Sc., for providing facilities in his research laboratories, his guidance and for his keen interest in the progress of the work and to Dr. J. Bhimasenachar, D.Sc., for many useful suggestions in the experiments. The author is also indebted to the Syndicate of the Andhra University for the award of a research scholarship.

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NUCLEAR OXIDATION IN THE FLAVONE SERIES

Part I. A New Synthesis of Gossypetin and 8-Hydroxy-Galangin

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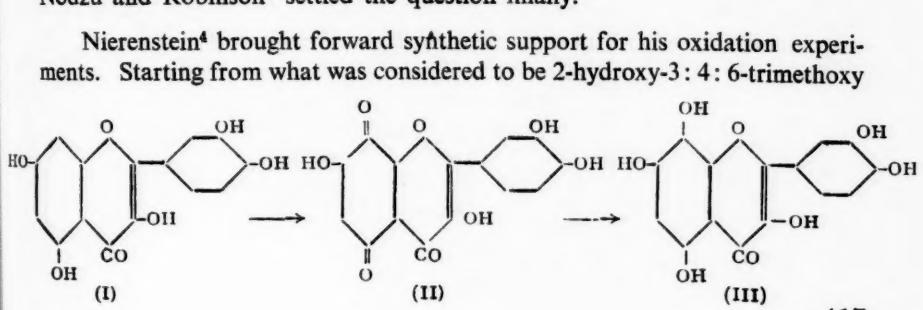
Received March 10, 1947

Robinson's theory of the Biogenesis of Anthocyanins and Anthoxanthins and its special application to the naturally occurring group of flavones and flavonols was discussed in an earlier publication.[1] In that connection it was necessary to provide experimental support regarding the possibility of nuclear oxidation taking place in these compounds. Attempts made by others in the past in this direction appear to have been unsuccessful.

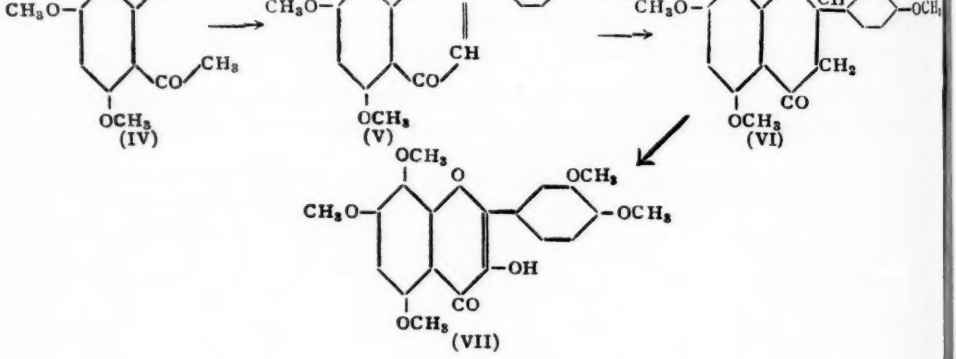
As early as 1911 when anthocyanins were still considered to be oxidation products of hydroxy-flavones, Nierenstein and Wheldale[2] subjected quercetin (I) to oxidation with chromic acid in acetic acid solution in the cold in order to obtain an anthocyanin-like substance. The deep red product was called quercetone and given the acceptable 5 : 8-quinone structure (II). By subjecting it to reductive acetylation and subsequently hydrolysing the intermediate acetate they obtained what was considered to be 8-hydroxy-quercetin (III) and degradation experiments showed that the side phenyl nucleus was unaffected. But the properties of the compound were different from those of gossypetin and quercetagetin. It melted at 352–53° and was insoluble in chloroform, acetone and pyridine and gave with cold alkali only a yellow colour. Its penta-methyl ether melted at 147–49° and the hexamethyl ether at 142–43°. This work threw into some confusion the constitution of gossypetin and quercetagetin till the classical paper of Baker, Nodzu and Robinson[3] settled the question finally.

Nierenstein[4] brought forward synthetic support for his oxidation experiments. Starting from what was considered to be 2-hydroxy-3 : 4 : 6-trimethoxy



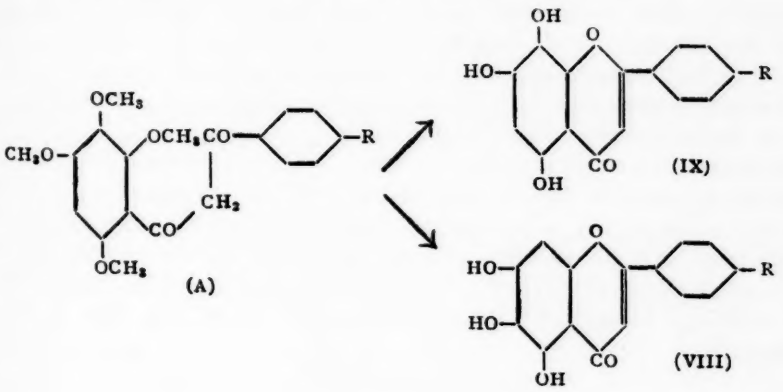
acetophenone and adopting Kostanecki's method of synthesis he prepared 8-hydroxy-quercetin which was found to be identical with his oxidation product. However in view of the later work of Baker *et al.*[3] establishing the constitution of gossypetin and quercetagetin by synthesis, it was definite that Nierenstein's oxidation had gone wrong. Even the straight-forward method of synthesis failed in his hands for the reason given below. It appears to be a further error that the final products from the two methods were considered to be identical. For the failure of the synthesis the starting ketone (IV) for which he gave a melting point of 125–26° and which was prepared by a method not free from ambiguity seems to have been primarily responsible. Recently we had occasion to carry out this synthesis since the pentamethyl gossypetin (VII) with the 3-hydroxyl free was required in connection with the constitution of gossypin. The required ketone was obtained by an unambiguous method (Sastri and Seshadri)[5] and it melted at 113–14°. The synthesis went smoothly yielding a gossypetin derivative. The following table gives a comparison of the various compounds obtained by Nierenstein and by us:

Name of the compound	Nierenstein's data	Ours
1 2-hydroxy-3:4:6-trimethoxy-acetophenone (IV)	125–26°	113–14°
2 Chalkone (V) ..	143°	143–45°
3 Acetate of chalkone ..	168°	135–36°
4 Flavanone (VI) ..	186–87°	175–76°
5 Flavonol (VII) ..	147–49°	228–30°
6 Fully methylated ether of (VII) ..	142–43° (different from hexa-methyl-gossypetin)	170–72° (identical with hexa-methyl gossypetin)



Another error which seems to have passed unnoticed, was present in the above work of Nierenstein. He reported that the pentamethoxy-flavonol (VII) was found to be identical with the pentamethyl-ether obtained by the partial methylation of his hydroxy-quercetin using dimethyl sulphate and alkali. This involved the idea that the particular hydroxyl in flavonols which was resistant to methylation was the one located in the 3-position. It was obviously wrong since even in flavones having no hydroxyl in the 3-position this characteristic had been observed. It is now well known that the 3-hydroxyl is in fact readily methylated and the resistant hydroxyl is present in the 5-position.

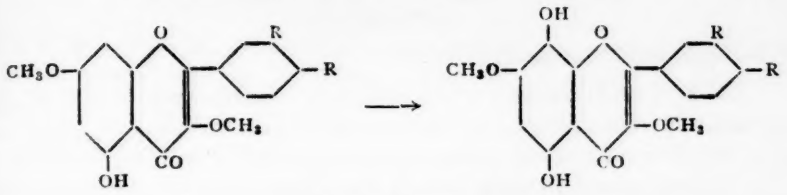
Nierenstein's[6] oxidation of chrysin to chrysone and its subsequent conversion to hydroxy chrysin seems to have met with no better success. The hydroxy-chrysin melted at 304–05° and its properties showed no agreement with those of norwogonin.[5,7] However, earlier this experiment was used for arriving at the correct constitution of scutellarein. Bargellini[8] synthesised scutellarein by heating with hydroiodic acid 2:3:4:6:4′-pentamethoxy-dibenzoylmethane (A, R = OCH_3). Of the two possible constitutions for the product he preferred the 5:6:7-arrangement (VIII, R= OH) based on certain analogies. In support of this he repeated the reaction using the simpler compound 2:3:4:6-tetramethoxy-dibenzoyl-methane (A, R = H) and for this product he definitely ruled out the 5:7:8-structure (IX, R = H) since it did not agree with the hydroxy-chrysin of Nierenstein in its properties. In order to provide further evidence for the constitution of scutellarein he[9] oxidised apigenin with chromic acid and reported the formation of a red substance probably analogous to chrysone. But the promised report of further work has not appeared so far.



More recently Venkataraman[10] reported that attempts made in his laboratory to oxidise chrysin and 5-hydroxy-6-benzyl-7-benzyloxy-flavone using chromic anhydride, nitric acid, potassium persulphate and selenium dioxide were unsuccessful; they did not lead to any homogeneous material other than the starting substances.

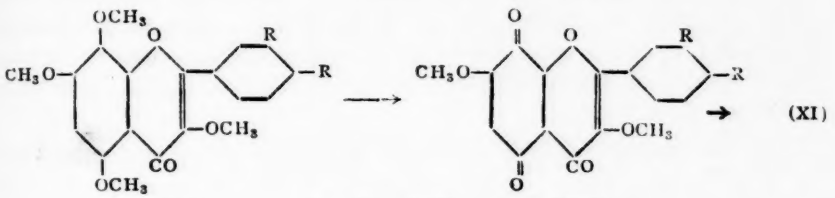
In spite of these failures the theory of biogenesis was so well supported from other directions that a reinvestigation of nuclear oxidation seemed to be justified. Potassium persulphate was chosen as the most convenient and direct reagent whose action is most closely approximating to biological nuclear oxidation. It is well established that this oxidising agent readily attacks the nuclear para position to an existing hydroxyl and introduces a fresh hydroxyl. As an intermediate stage a sulphate seems to be formed. Since this is soluble in water it is readily separated from impurities, particularly the unchanged material, and the oxidation product is then liberated by acid hydrolysis. It is clear that the oxidation involves anionoid (nucleophilic) activity of the concerned para position and the stages could be represented as given below taking the simplest phenol as example.

In the experiments described later in this paper the conversion of galangin and quercetin into 8-hydroxy-galangin and gossypetin has been achieved. Prior to oxidation, the 5:7-hydroxy-flavonols are converted into their partial methyl ethers leaving the hydroxyl in the 5-position alone free (X). This is intended to give protection to the molecule against general oxidation under the alkaline conditions employed. 3:7-O-dimethyl-galangin (X, R = H) and 3:7:3′:4′-O-tetramethyl-quercetin (X, R = OCH_3) are then oxidised with potassium persulphate. A difficulty arises here from the sparing solubility of these partial methyl ethers in aqueous alkali, but it has been got over by the judicious addition of pyridine. Satisfactory yields of the 5:8-dihydroxy compounds (XI) are obtained. These compounds give the characteristic reactions of quinols and readily yield the corresponding quinones by treatment with *p*-benzo quinone. Methylation with dimethyl sulphate in anhydrous acetone medium converts them into the tetramethyl ether of 8-hydroxy-galangin[11] (XII, R = H) and gossypetin hexamethyl ether[12] (XII, R = OCH_3) respectively and demethylation yields the free hydroxy flavonols.



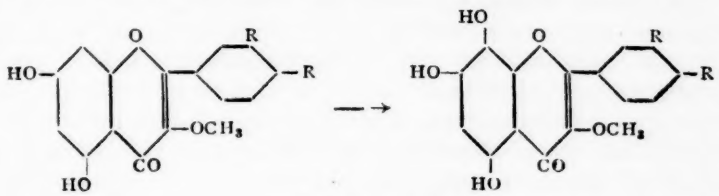
(X) R = H or OCH_3 (XI)

For purposes of comparison the 5: 8-quinones (XIII) and quinols (XI), have been prepared from authentic samples of the fully methylated ethers of 8-hydroxy-galangin and gossypetin (XII) by oxidation with nitric acid and subsequent reduction with sodium sulphite or sulphur dioxide.[13]



(XII) R = H or OCH_3 (XIII)

From the point of view of the easy synthetic preparation of these 5: 7: 8-hydroxy-flavonols, the oxidation of the dihydroxy compounds (XIV), galangin-3-methyl ether (R = H) and quercetin-3: 3′: 4′-trimethyl ether (R = OCH_3) becomes important, because these dihydroxy compounds form the earliest products of Allan-Robinson synthesis. Their oxidation has been found to proceed smoothly, their ready solubility in aqueous alkali being an added convenience. The products are trihydroxy compounds (XV) and are again obtained in good yields. This constitutes a remarkably easy method of synthesis of these 5: 7: 8-hydroxy-flavonols and makes them readily available for experimental purposes. Further it marks a stage in the attempt to minimise the protection of the hydroxyl groups before effecting oxidation and to approximate more closely to biogenetic conditions.



(XIV) R = H or OCH_3 (XV)

Experimental

5 : 8-Dihydroxy-3 : 7-dimethoxy-flavone

To a stirred solution of 5-hydroxy-3 : 7-dimethoxy-flavone (1 g.) in a mixture of pyridine (20 c.c.) and aqueous potassium hydroxide (1 g. in 25 c.c.) were added simultaneously aqueous potassium persulphate solution (2 g. in 100 c.c.) and aqueous potash (1 g. in 25 c.c.) dropwise during the course of two hours. After keeping the deep olive brown reaction mixture overnight it was neutralised to congo red and extracted twice with ether. The clear brown aqueous solution was then treated with sodium sulphite (2 g.) and concentrated hydrochloric acid (20 c.c.) and kept in a boiling water-bath for 30 minutes. The glistening brownish yellow crystalline solid that separated out was filtered off and washed well with water; some more of it was obtained by ether extracting the mother liquor; yield, 0.55 g. After recrystallisation from ethyl acetate it came out as bright yellow long and thin rectangular plates melting at 221–23° (Found: C, 65.3; H, 4.8; $C_{17}H_{14}O_6$ requires C, 65.0; H, 4.5%).

It was sparingly soluble in alcohol and ethyl acetate and moderately in glacial acetic acid. It was not easily soluble in sodium carbonate solution. In 5% aqueous sodium hydroxide it readily dissolved to give a deep red solution which changed to bluish-violet in a few minutes. With ferric chloride in alcoholic solution it gave a pale green colour which quickly changed to brown and with *p*-benzoquinone a red solution was obtained which slowly deposited an orange red crystalline solid.

The dihydroxy compound (0.2 g.) was acetylated with acetic anhydride (3 c.c.) and a few drops of pyridine. The acetate crystallised from alcohol in the form of colourless matted soft needles melting at 191–93°. It was sparingly soluble in alcohol but readily in chloroform.

A solution of the dihydroxy compound (0.2 g.) in dry acetone (20 c.c.) was treated with dimethyl sulphate (0.5 c.c.) and anhydrous potassium carbonate (5 g.). After refluxing for 6 hours the solvent was distilled off and the residue treated with water. The pale brown solid that separated out was filtered, washed and crystallised from a mixture of benzene and ligroin from which it separated out as colourless rectangular prisms melting at 162–64° identical with 3 : 5 : 7 : 8-tetramethoxyflavone[11]; the mixed melting point was undepressed. The dihydroxy compound was demethylated by means of boiling hydriodic acid. The product crystallised from ethyl acetate in the form of fibrous needles melting at 231–33°. It gave all the reactions of 8-hydroxy galangin[11] and the mixed melting point was undepressed. The acetate was also prepared. It crystallised from dilute

alcohol as colourless narrow rectangular prisms and melted at 173–74° alone or mixed with an authentic sample of the acetate of 8-hydroxy-galangin.

3: 7-*Dimethoxy-flavoquinone*

3: 5: 7: 8-Tetramethoxy-flavone (0.2 g.) was treated with nitric acid (d. 1.25; 5 c.c.) with vigorous stirring. On keeping for 15 minutes at 15–20° the solid dissolved to a yellow solution which changed to orange and finally red and a deep red product separated out which soon solidified. It was filtered, washed with nitric acid (d. 1.25) followed by water thoroughly and dried. Crystallised twice from alcohol it separated out as shining orange-red rectangular plates and prisms melting at 220–21° (Found: C, 65.4; H, 4.0; $C_{17}H_{12}O_6$ requires C, 65.4; H, 3.8%). It was sparingly soluble in alcohol. In aqueous sodium hydroxide it readily dissolved to a bluish-violet solution.

A solution of the above quinone (0.1 g.) in glacial acetic acid (0.5 c.c.) was treated with sodium sulphite (0.5 g.). The deep red solution immediately changed to bright yellow. On dilution with water a yellow solid separated out which was filtered, washed and crystallised from alcohol from which it came out in the form of golden yellow shining rectangular plates melting at 221–23° alone or in admixture with the quinol prepared by the oxidation of 5-hydroxy-3: 7-dimethoxy-flavone.

5: 7: 8-*Trihydroxy*-3-*methoxy-flavone*

A stirred solution of 5: 7-dihydroxy-3-methoxy-flavone (1 g.) in aqueous potassium hydroxide (0.75 g. in 25 c.c.) was slowly treated with a solution of potassium persulphate (2 g. in 100 c.c. of water) and aqueous potash (0.75 g. in 25 c.c.) simultaneously during the course of 2 hours while keeping the reaction mixture at a temperature of 15–20°. After allowing the deep brown solution to stand for 24 hours at room temperature, it was neutralised (Congo Red) and the brown solid that separated out was removed by extraction with ether twice. The clear brown aqueous layer was treated with sodium sulphite (2 g.) and concentrated hydrochloric acid (20 c.c.) and kept in a boiling water-bath for 30 minutes. A yellow solid began to separate during the course of the heating and on cooling more of it was obtained. It was filtered and washed free from acid; ether extraction of the mother liquor yielded some more of the substance; yield 0.5 g. It crystallised from a mixture of absolute alcohol and benzene in the form of tiny yellow prisms melting at 245–47° (Found: C, 64.1; H, 4.3; $C_{16}H_{12}O_6$ requires C, 64.0; H, 4.0%).

It was readily soluble in alcohol, acetone or ethyl acetate and sparingly in ether. In 5% aqueous sodium hydroxide it dissolved to a deep brown-red solution which changed rapidly to pale blue on shaking with air. With 5% sodium carbonate the solution was yellowish-brown changing to pale yellow. In alcoholic solution it gave a deep reddish-brown colour with ferric chloride, a yellow precipitate with lead acetate and a red colour with *p*-benzoquinone with a gradual separation of a reddish-brown solid.

The substance (0.2 g.) on acetylation with acetic anhydride (3 c.c.) and a few drops of pyridine gave rise to the acetyl derivative which crystallised from a mixture of benzene and ligroin in the form of colourless thin plates melting at 195–97°.

On methylation with dimethyl sulphate (0.5 c.c.) and anhydrous potassium carbonate (5 g.) in anhydrous acetone medium the trihydroxy compound yielded the methyl ether which crystallised from benzene-petroleum ether mixture in the form of colourless thick rectangular prisms melting at 162–64°. Mixed melting point with an authentic sample of 3: 5: 7: 8-tetramethoxy-flavone was not depressed.

5: 8-*Dihydroxy*-3: 7: 3′: 4′-*tetramethoxy-flavone*

A stirred solution of 5-hydroxy-3: 7: 3′: 4′-tetramethoxy-flavone (1 g.) in a mixture of pyridine (20 c.c.) and aqueous potash (0.5 g. in 25 c.c.) was treated with aqueous potassium persulphate (1.5 g. in 50 c.c. of water), and potassium hydroxide solution (0.5 g. in 25 c.c.) during the course of two hours. After leaving the deep olive green solution for 24 hours it was neutralised with concentrated hydrochloric acid and the solid which separated out was extracted with ether. The clear brown aqueous layer was heated on a boiling water-bath for 30 minutes after the addition of sodium sulphite (2 g.) and concentrated hydrochloric acid (20 c.c.). The yellow crystalline solid that was deposited was filtered off and washed; some more of it was obtained on extracting the mother liquor with ether; yield, 0.45 g. When crystallised twice from ethyl acetate it separated in the form of lustrous golden yellow thick rectangular prisms melting at 250–52° (Found: C, 60.6; H, 4.6; $C_{19}H_{18}O_8$ requires C, 61.0; H, 4.8%).

It was sparingly soluble in alcohol and ethyl acetate and moderately soluble in glacial acetic acid. It was not easily soluble in sodium carbonate. In 5% aqueous sodium hydroxide it readily dissolved to a deep red solution which changed to bluish-violet in a few minutes. In alcoholic solution it gave with ferric chloride a transient green colour which quickly changed to brown; with *p*-benzoquinone a red colour was produced and a deep red solid slowly separated out.

The dihydroxy compound (0.1 g.) was methylated using dimethyl sulphate (0.5 c.c.) and anhydrous potassium carbonate (5 g.) in dry acetone medium. The methyl ether crystallised from alcohol in the form of colourless needles metling at 170–72° alone or in admixture with the hexamethyl ether of gossypetin.

A solution of the dihydroxy compound (0.2 g.) in dry acetone (25 c.c.) was treated with ethyl iodide (0.5 c.c.) and anhydrous potassium carbonate (5 g.). After refluxing for 12 hours the solvent was completely removed, the residue treated with water and the white solid which separated out was filtered off. On crystallisation from alcohol the diethyl ether separated out in the form of colourless narrow rectangular plates melting at 143–45° (Found: C, 61.3; H, 6.3; $C_{23}H_{26}O_8$, H_2O requires C, 61.6; H, 6.3%). It was readily soluble in alcohol, benzene or acetone, and insoluble in sodium hydroxide.

5: 7: 8-*Trihydroxy*-3: 3′: 4′-*trimethoxy-flavone*

To a stirred solution of 5: 7-dihydroxy-3: 3′: 4′-trimethoxy-flavone (1 g.) in aqueous potassium hydroxide (0.5 g. in 25 c.c.) were added dropwise potassium persulphate solution (1.5 g. in 50 c.c.) and aqueous potash (0.5 g. in 25 c.c.) during the course of 2 hours. After keeping the deep brown solution for 24 hours it was neutralised with hydrochloric acid and extracted twice with ether. The clear brown aqueous layer was treated with sodium sulphite (2 g.) and concentrated hydrochloric acid (20 c.c.). On heating the solution at 100° for 30 minutes a yellow solid separated out which was filtered and washed; some more of it was obtained by extracting the mother liquor with ether; yield, 0.45 g. On crystallisation from alcohol it separated in the form of yellow microscopic prisms melting at 244–46°. (Found: C, 57.2; H, 4.9; $C_{18}H_{16}O_8$, H_2O requires C, 57.2; H, 4.8%). It was easily soluble in alcohol and the solution gave a deep greenish brown colour with ferric chloride, a yellow precipitate with lead acetate and a red colour with *p*-benzoquinone. In 5% aqueous sodium hydroxide it readily dissolved to a deep brown red solution; the colour faded rapidly to a pale blue which was fairly stable. With aqueous sodium carbonate the initial brown-red faded to a pale yellowish-green.

The trihydroxy compound (0.1 g.) was methylated in anhydrous acetone medium with dimethyl sulphate (0.5 c.c.) and anhydrous potassium carbonate (5 g.). The methyl ether crystallised from alcohol in the form of colourless needles melting at 170–72°. The mixed melting point with an authentic sample of hexamethyl gossypetin was not depressed.

Summary

Nuclear oxidation leading to the preparation of 8-hydroxy-galangin and gossypetin has been carried out. 3:7-dimethyl-ether of galangin and 3:7:3′:4′-tetramethyl-ether of quercetin have been oxidised by means of potassium persulphate to the corresponding 5:8-dihydroxy-compounds (quinols). Even the 5:7-dihydroxy-compounds, 3-O-methyl-galangin and 3:3′:4′-O-trimethyl-quercetin could be oxidised to the corresponding 5:7:8-trihydroxy-derivatives in good yields. Subsequent methylation yields the fully methylated ethers of 8-hydroxy-galangin and gossypetin and demethylation the free hydroxy flavonols. These experiments not only illustrate facile nuclear oxidation in the flavone series in support of the theory of biogenesis, but also constitute simple and elegant methods for the synthesis of 5:7:8-hydroxy-flavonols.

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NUCLEAR OXIDATION IN THE FLAVONE SERIES

Part II. Synthesis of Norwogonin and Isowogonin

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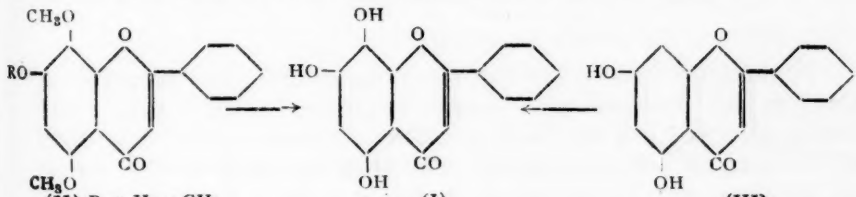
Received March 18, 1947

As already mentioned in Part I[1] attempts made by previous workers to effect nuclear oxidation of chrysin (III) were not successful. It is an important reaction since, apart from biogenetic interest, it will lead to an easy synthesis of norwogonin (I), a flavone having the 5:7:8-arrangement of hydroxyl groups. This compound was prepared in the past by methods involving the demethylation of its methyl ethers (II). Hydriodic acid could not be used for this purpose since it brings about re-arrangement in the molecule leading to the formation of 5:6:7-trihydroxy-flavone (baicalein). Aluminium chloride has been found to be free from this defect. Norwogonin was thus prepared by Shah *et al.*[2] by the demethylation of 5:8-dimethoxy-7-hydroxy-flavone (II, R = H) with aluminium chloride in nitrobenzene solution and by Sastri and Seshadri[3] by the demethylation of 5:7:8-trimethoxy-flavone (II, R = CH_3) using benzene solution. But it is our experience that this reagent does not always give consistent yields. Consequently a method of synthesis which does not involve demethylation will be the most satisfactory.

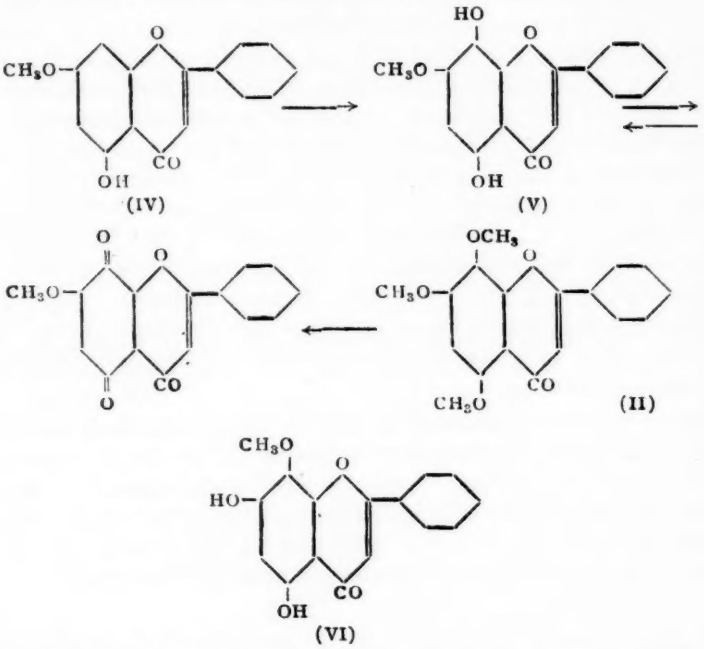
It has now been found that chrysin (III) could be oxidised smoothly by means of alkaline persulphate to norwogonin (I), the product agreeing in all respects with the synthetic sample of Sastri and Seshadri.[3] This result definitely confirms that aluminium chloride demethylation is free from the possibility of isomerisation. The properties of this compound are very different from those of hydroxy-chrysin reported by Nierenstein.[7]



(II) R = H or CH_3 (I) (III)

The oxidation of tecto-chrysin (7-monomethyl-ether of chrysin, IV) has also been carried out with persulphate. It gives rise to the 7-methyl-ether (V) of norwogonin. This is different in its properties from wogonin and hence offers further support to the accepted constitution of wogonin as the 8-mono-methyl-ether (VI). The new compound is therefore named iso-wogonin (V).

In connection with the constitution of gossypin[4] it has recently been shown that gossypetin-hexamethyl-ether undergoes smooth conversion into gossypetone tetramethyl ether by treatment with nitric acid, and reduction of the quinone yields the 5:8-dihydroxy-compound. This process of oxidative demethylation has also been employed now for the preparation of isowogonin (V) from 5:7:8-trimethoxy-flavone[3] (II, $R = CH_3$). The samples obtained by the two methods are found to be identical.



In preparing chrysin for the above experiments the procedure of Robinson and Venkataraman[5] frequently yields a product with a low melting point and it is obviously a mixture. Ordinary crystallisation from alcohol does not effect a separation. By using a mixture of ethyl acetate and petroleum ether the less soluble fraction is found to be chrysin but the

yield is poor. The remaining portion which seems to be mainly 3-benzoyl-chrysin[6] could be converted into chrysin by boiling with 5% aqueous sodium carbonate for 2 hours. Giving this treatment to the crude mixture itself a yield of about three grams of almost pure chrysin could be obtained from 5 grams of phloroacetophenone. Partial methylation of chrysin leading to the formation of tectochrysin is readily effected by using the correct amount of dimethyl sulphate and potassium carbonate in anhydrous acetone medium.

Experimental

Oxidation of chrysin to norwogonin.—A stirred solution of chrysin (0·9 g.) in aqueous potassium hydroxide (1·2 g. in 25 c.c.) was gradually treated with potassium persulphate solution (1·2 g. in 50 c.c.) during the course of two hours. The deep brown solution was left for 24 hours and then rendered slightly acidic to Congo Red. The brown solid that separated out was filtered off and the filtrate extracted twice with ether. The aqueous layer was treated with sodium sulphite (3 g.) and concentrated hydrochloric acid (25 c.c.) and kept at 90° for 30 minutes. A yellow solid began to separate out. After cooling, it was filtered and washed well with water. On extracting the filtrate with ether some more of the substance could be obtained. Yield 0·4 g. On crystallisation from a mixture of ethyl acetate and petroleum ether the product separated out in the form of golden yellow rectangular plates and prisms melting at 258–60° alone or in admixture with an authentic sample of norwogonin.[3] It was soluble in acetone. In aqueous sodium carbonate (5%) it readily dissolved to a brown coloured solution while in aqueous sodium hydroxide it gave a deep reddish brown colour changing to pale blue. In alcoholic solution it gave with ferric chloride a pale green colour which changed to deep reddish brown.

The oxidation product (0·1 g.) was acetylated by boiling with acetic anhydride (2 c.c.) and a few drops of pyridine for 1 hour. After distilling off the reagents under reduced pressure the residual white solid was crystallised from ethyl acetate when it separated out as colourless narrow rectangular plates melting at 225–27°. Mixed melting point with the triacetate of norwogonin was not depressed.

A solution of norwogonin (0·1 g.) in dry acetone (20 c.c.) was methylated using dimethyl sulphate (0·5 c.c.) and anhydrous potassium carbonate (5 g.). The methyl ether crystallised from a mixture of benzene and petroleum ether in the form of colourless needles melting at 167–68°. Mixed melting point with an authentic sample of 5:7:8-trimethoxy-flavone was undepressed.

Nierenstein's description[7] of hydroxy-chrysin is as follows: m.p. of the substance, 304–5°; does not dissolve in acetone and gives a yellow colour with cold alkali; m.p. of acetate 214–17°.

Tectochrysin.—A solution of chrysin (1·3 g.) in anhydrous acetone (100 c.c.) was refluxed with dimethyl sulphate (0·55 c.c.) and anhydrous potassium carbonate (5 g.) for 6 hours. After distilling off the solvent the residue was treated with water. The undissolved solid was filtered, washed and crystallised from alcohol from which it separated out as pale brown needles melting at 165–66°. Yield 1 g.

Oxidation of tectochrysin to isowogonin.—To a stirred solution of tectochrysin (1 g.) in a mixture of pyridine (20 c.c.) and aqueous potassium hydroxide (1 g. in 25 c.c.) was added a solution of potassium persulphate (1·5 g. in 50 c.c.) during the course of two hours. The deep greenish brown solution, after keeping for 24 hours, was neutralised with hydrochloric acid and the pale brown precipitate was removed by filtration. This was found to be almost pure tectochrysin and some more of it was obtained by ether extracting the filtrate twice. The clear brown filtrate was then treated with sodium sulphite (3 g.) and concentrated hydrochloric acid (25 c.c.) and heated on a boiling water-bath for 30 minutes. The yellow solid that separated out was filtered and the filtrate extracted with ether; the ether extract gave some more of the yellow substance. Total yield was 0·45 g. After crystallisation from ethyl acetate it came out as bright yellow soft needles melting at 234–35°. (Found: C, 67·4; H, 4·0; $C_{16}H_{12}O_5$ requires C, 67·6; H, 4·2%.)

It was sparingly soluble in alcohol, ether and benzene. In alcoholic solution, with a drop of ferric chloride it gave a green colour which rapidly turned brown particularly with excess of the reagent. In aqueous sodium hydroxide it readily dissolved to a deep reddish brown solution. When treated with *p*-benzoquinone in alcoholic solution an orange coloured flavoquinone slowly crystallised out; after recrystallisation from ethyl acetate it came out as rectangular plates and melted at 245–47°.

Isowogonin (0·1 g.) was acetylated by boiling with acetic anhydride (3 c.c.) and a few drops of pyridine for 1 hour. The acetate crystallised from ethyl acetate in the form of colourless narrow rectangular plates melting at 230–32°.

Isowogonin (0·1 g.) when methylated in dry acetone medium (20 c.c.) with dimethyl sulphate (0·5 c.c.) and potassium carbonate (5 g.) yielded the dimethyl ether which crystallised from a mixture of benzene and petroleum ether as colourless needles melting at 167–68°; the mixed melting point with 5:7:8-trimethoxy flavone was undepressed.

Oxidative demethylation of 5:7:8-*trimethoxy-flavone.*—5:7:8-Trimethoxy-flavone (0.2 g.) was treated with nitric acid (5 c.c.; d. 1·25) followed by vigorous stirring. The solid slowly went into solution giving a yellow colour and soon an orange coloured solid crystallised out. After keeping for 30 minutes, it was filtered, washed well with nitric acid (d. 1·25) followed by water. Crystallisation from acetone yielded the flavo-quinone in the form of orange coloured rectangular plates melting at 245–47°. It was very sparingly soluble in alcohol and acetone. It readily dissolved in aqueous sodium hydroxide to a bluish violet solution.

A solution of the quinone (0·1 g.) in glacial acetic acid (1 c.c.) was treated with sodium sulphite (0·5 g.). The mixture was heated for a minute and diluted with water. The bright yellow solid was filtered, washed and crystallised from ethyl acetate when it separated out as golden yellow soft needles melting at 235–36° alone or in admixture with a sample of isowogonin prepared by the direct oxidation of tectochrysin.

In some experiments the flavoquinone was accompanied by some impurity which was difficult to remove by crystallisation and the product sintered markedly below the melting point. But after reduction the sample of isowogonin could be more easily purified by crystallisation.

Summary

The nuclear oxidation of chrysin and tectochrysin has been successfully effected using potassium persulphate. The first yields norwogonin and the second the 7-methyl-ether now named isowogonin. The method of oxidative demethylation of the 5- and 8-positions has also been employed for the preparation of isowogonin from 5:7:8-trimethoxy-flavone.

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NUCLEAR OXIDATION IN THE FLAVONE SERIES

Part III. A New Synthesis of Primetin

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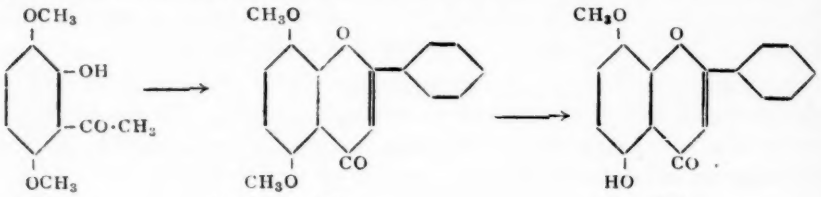
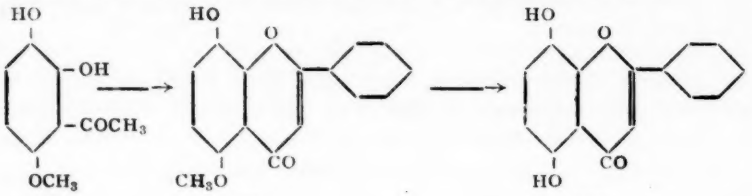
Primetin is an important member of the flavone group and is the only representative with the 5: 8-arrangement of hydroxyl groups in the molecule, the hydroxyl in the 7-position being unusually absent. The dimethyl ether (II) and monomethyl ether (III) were synthesised by Baker *et al.*[1] as follows:



(I) (II) (III)

The dimethyl ether was the first product of flavone ring closure starting from the ketone (I). Partial demethylation with aluminium chloride in ether solution gave rise to the monomethyl ether (III). Complete demethylation using hydrobromic acid did not yield primetin since this reagent brought about rearrangement also producing 5: 6-dihydroxy flavone. Other methods employed by the above workers were also unsuccessful. This difficulty was got over by Nakazawa[2] by employing 2: 3-dihydroxy-6-methoxy acetophenone (IV) for the synthesis and finally demethylating the methoxyl in the 5-position with aluminium chloride giving rise to primetin (VI).



(IV) (V) (VI)

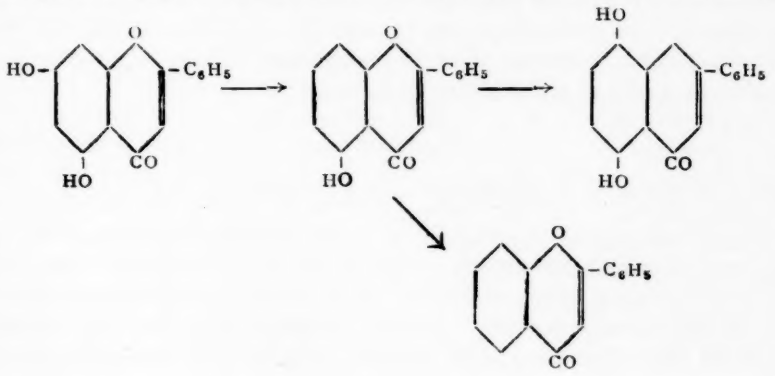
In a recent publication[3] from this laboratory it was recorded that anhydrous aluminium chloride in dry benzene medium brings about smooth

demethylation of 5:7:8-trimethoxyflavone to norwogonin. This method has now been applied to primetin dimethyl ether with good success and pure samples of primetin obtained.

Plants belonging to the genus *Primula* appear to be as important in connection with the flavones as in the study of the anthocyanins. The occurrence of flavone, the fundamental compound of the group, as a characteristic dust, called ' meal ' or ' farina ' by gardeners, on the flower stalks, leaves and seed capsules of many species of the *Primula* was first recorded by Müller.[4] Primetin was isolated by Nagai and Hattori[5] from the leaves of the Japanese *P. modesta*; it was present along with flavone. More recently, from the deposit formed on the stalks and blossoms of *P. imperialis*, Karrer and Schwab[6] isolated some 5-hydroxy flavone though flavone itself was the main component. These compounds are unique for these plants and have not been found elsewhere.

In the course of his study of the farina from twenty-one species of *Primula*, Blasdale[6] found that all of them contained flavone as the main component. However, from *P. denticulata* he isolated in a very small yield an orange-yellow dihydroxy-flavone melting at 228° and forming an acetate with the melting point at 183–84° and from *P. verticillata* a yellow crystalline substance melting at 153° and having the molecular formula $C_{15}H_{10}O_3$. Though he did not identify them, it may here be pointed out that the properties of the dihydroxy-flavone agree with those of primetin and that the second compound resembles 5-hydroxy-flavone.

In an earlier paper by Rao and Seshadri[7] was suggested the possibility of the formation of primetin in the plant from 5:7-dihydroxy-flavone through 5:7:8-trihydroxy flavone as an intermediate stage. The above mentioned discovery of 5-hydroxy-flavone seems to suggest the alternative course through



5-hydroxy-flavone as more probable. This is supported by the ready oxidation of 5-hydroxy-flavone directly into primetin by means of alkaline persulphate as described later in this paper and it constitutes the simplest and the most direct synthesis of this interesting flavone. The substance behaves like any other quinol and undergoes conversion into the corresponding quinone readily. Its dimethyl ether is identical with 5: 8-dimethoxy-flavone prepared by the method of Baker *et al.*[1]

5-Hydroxy-flavone was first prepared by Sugasawa[8] by the fusion of γ-resacetophenone with benzoic anhydride and sodium benzoate at 180–90°. He reported that the use of a higher temperature gave a high percentage of the 3-benzoyl derivative. Later Baker[9] reported that the yield of 5-hydroxy-flavone by the above method was unsatisfactory and sought an alternative route to the compound in the molecular rearrangement of 2: 6-dibenzoyloxy acetophenone in toluene in presence of potassium carbonate. The reaction yielded directly the 3-benzoyl-5-hydroxy-flavone in poor yield and though this could be hydrolysed to 5-hydroxy-flavone conveniently by means of aluminium chloride in nitrobenzene solution the method was considered to be inferior to the first. More recently Trivedi, Sethna and Shah[10] benzoylated 2-acetyl resorcinol using excess of sodium benzoate and benzoic anhydride and heating for 9 hours at 180–90°. They isolated 5-benzoyloxy-3-benzoyl flavone as the primary product and by effecting hydrolysis in stages obtained 5-hydroxy-3-benzoyl-flavone and 5-hydroxy-flavone. In our attempts to prepare this substance it was found that a good yield of 3-benzoyl-5-hydroxy-flavone could be obtained using the ordinary conditions of the Allan-Robinson reaction and this could be conveniently converted into 5-hydroxy-flavone by boiling with aqueous alcoholic sodium carbonate for 2 hours. As an independent check we have also prepared it by another method. Starting with the monomethyl-ether of γ-resacetophenone and adopting the Baker-Venkataraman procedure, 5-methoxy-flavone has been made and demethylated to yield 5-hydroxy-flavone. The samples obtained by the two methods are found to be identical.

Experimental

Demethylation of 5: 8-*dimethoxy-flavone to primetin.*—

A solution of 5: 8-dimethoxy-flavone[1] (0·15 g.) in dry benzene (10 c.c.) was treated with a suspension of finely powdered anhydrous aluminium chloride (0·5 g.) in benzene (10c.c.). The mixture was gently refluxed for 45 minutes on a water-bath. A dark red aluminium chloride complex separated out. The supernatant benzene solution was decanted off into

a porcelain basin and the residue in the flask washed again with a little more benzene. Crushed ice and hydrochloric acid were added to the reddish brown residue and stirred well. To complete the decomposition of the complex the mixture was heated in a boiling water-bath for 15 minutes. The yellow crystalline product was then filtered off and washed well with water. It was recrystallised from ethyl acetate from which it separated in the form of golden yellow rectangular plates melting at 230–32°. Yield 0·1 g. It was easily soluble in alcohol, acetone and ethyl acetate and sparingly in benzene and ether. In alcoholic solution it gave a green colour with a drop of ferric chloride and the colour changed to brown on the addition of more of the reagent. In aqueous sodium hydroxide it readily dissolved giving a red colour. With *p*-benzoquinone in alcoholic solution it developed a red colour. Mixed melting point with 5: 8-dihydroxy-flavone obtained by the direct oxidation of 5-hydroxy-flavone was undepressed.

5-*Methoxy-flavone*.—

2-Hydroxy-6-methoxy acetophenone (2 g.) was dissolved in anhydrous pyridine (8 c.c.) and treated with benzoyl chloride (2.1 c.c.) and the solution heated in a boiling water-bath for one hour. It was then cooled, poured into dilute hydrochloric acid and the product extracted twice with ether. The ether extract was washed successively with hydrochloric acid, aqueous sodium carbonate, aqueous sodium hydroxide and water. When it was finally dried over calcium chloride and the solvent distilled off, the benzoate was obtained as a pale yellow viscous oil; yield 2·5 g.

A solution of the 2-benzoyloxy-6-methoxy acetophenone (2 g.) in anhydrous toluene (15 c.c.) was treated with finely powdered sodamide (6 g.) and the mixture kept at 100° for 4 hours. The solid as well as the supernatant solution assumed a deep yellow colour and in the initial stages vigorous evolution of ammonia was noticed. The contents were then filtered under suction, and washed well with dry benzene. The dry residue was then dropped into ice-water (60 c.c.) in small lots with vigorous stirring and the yellowish brown solution saturated with carbon dioxide when a yellow semi-solid mass separated. It was extracted with ether, the ether solution dried over sodium sulphate and the solvent distilled off when a bright red viscous oil was left behind. The toluene filtrate provided some more of the same substance when extracted with alkali and the alkali solution saturated with carbon dioxide followed by ether extraction. The diketone dissolved in aqueous sodium hydroxide to a yellow solution and a yellow sodium salt separated out soon. In alcoholic solution a reddish brown colour was obtained with ferric chloride.

A mixture of the above diketone (2 g.), glacial acetic acid (15 c.c.) and freshly fused sodium acetate (2 g.) was kept gently refluxing for 4 hours. It was then cooled and diluted with water (100 c.c.). The white crystalline solid that separated out was filtered off and washed with water. Crystallisation of the substance from a mixture of benzene and petroleum-ether gave colourless rectangular prisms and plates melting at 130–31° (Found: C, 75·9; H, 4·5; $C_{16}H_{12}O_3$ requires C, 76·2; H, 4·8%.). Yield 1·5 g.

5-*Hydroxy-flavone.*—

(*a*) 5-Methoxy-flavone (1·5 g.) was dissolved in acetic anhydride (10 c.c.) and the solution cautiously treated with hydriodic acid (20 c.c.). After gently refluxing the resulting deep brown solution for one hour it was cooled, poured into water (100 c.c.) and treated with sufficient sodium sulphite to remove iodine. The yellow product was filtered, washed with water and crystallised from ethyl acetate when it separated out as pale yellow lustrous needles melting at 158–60°. It gave a purple colour with ferric chloride and was very sparingly soluble in aqueous sodium hydroxide. Yield 1 g.

(*b*) An intimate mixture of 2-acetyl resorcinol (2 g.) benzoic anhydride (10 g.) and sodium benzoate (3 g.) was heated under reduced pressure at 180–90° for 4 hours. The product when worked up as usual and crystallised from alcohol, came out as pale yellow needles melting at 177–78°. Yield 2 g.

The above 3-benzoyl derivative (1 g.) was gently refluxed with (1 : 1) aqueous alcoholic sodium carbonate (5%, 50 c.c.) for 2 hours. The alcohol was removed under reduced pressure, the alkaline solution acidified and the brown solid filtered and crystallised from alcohol-ethyl acetate mixture. It separated out as pale yellow needles melting at 158–60°. Yield 0·45 g.

5 : 8-*Dihydroxy-flavone*: *Primetin.*—

A stirred solution of 5-hydroxy-flavone (1 g.) in a mixture of pyridine (20 c.c.) and aqueous potassium hydroxide (1·2 g. in 20 c.c.) was slowly treated with aqueous potassium persulphate (1·7 g. in 50 c.c.) in the course of 2 hours. The greenish brown solution was allowed to stand for 24 hours and acidified when unchanged 5-hydroxy-flavone separated out; it was filtered and washed, quantity recovered being 0·3 g. The filtrate was extracted twice with ether and the clear brown aqueous layer treated with sodium sulphite (3 g.) and concentrated hydrochloric acid (25 c.c.) and kept in a boiling water-bath for 30 minutes. The yellow crystalline solid which separated out was filtered and washed with water. The filtrate on

ether extraction provided some more of the substance. Total yield was 0·45 g. When recrystallised from ethyl acetate it separated out in the form of golden yellow rectangular plates and prisms melting at 230–32° (Found: C, 70·5; H, 4·2; $C_{15}H_{10}O_4$ requires C, 70·9; H, 3·9%). In all its properties and reactions it was identical with the sample obtained by the demethylation of 5:8-dimethoxy flavone reported earlier.

The dihydroxy compound (0·3 g.) was methylated in anhydrous acetone medium (25 c.c.) with dimetyl sulphate (0·5 c.c.) and potassium carbonate (5 g.) by refluxing for 6 hours. The solvent was distilled off and the residue treated with water when a pale brown solid was left behind which was filtered and washed with water. It crystallised out from a mixture of benzene and petroleum ether in the form of colourless rectangular plates melting at 144–45°. Mixed melting point with an authentic sample of 5:8-dimethoxy flavone prepared according to the method of Baker, Brown and Scott[1] was undepressed. It was insoluble in aqueous alkali and did not give any colour with ferric chloride in alcoholic solution.

Summary

The difficulty of the demethylation of synthetic primetin dimethyl ether into primetin has been solved by the use of anhydrous aluminium chloride in benzene medium. The possibility of the formation of primetin in the Primula through the intermediate stage of 5-hydroxy-flavone is suggested. This is supported by a new synthesis of primetin in which the nuclear oxidation of 5-hydroxy-flavone is effected by means of persulphate. 5-Hydroxy-flavone required for these experiments has been prepared by independent methods.

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SYNTHETICAL EXPERIMENTS IN THE CHROMONE GROUP

Part XXI. Synthesis of Gentisin, the Colouring Matter of Gentian Root

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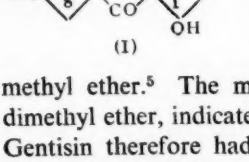
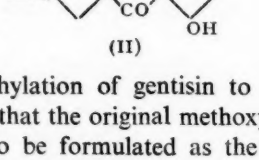
GENTISIN, the yellow colouring matter of *Gentiana lutea* (gentian root) was first isolated by Henry and Caventou,[1] and was shown by Baumert[2] to possess the formula $C_{14}H_{10}O_8$. Hlaiswetz and Habermann[3] demonstrated the presence of two hydroxyl groups and one methoxyl; but when fused with potassium hydroxide, it gave phloroglucinol and gentisic acid. Kostanecki[4] by demethylation of gentisin with hydriodic acid, showed it to be a monomethyl ether of gentisein, 1:3:7-trihydroxyxanthone (I), which was synthesised by Kostanecki and Tambor[5] by the distillation of gentisic acid and phloroglucinol in presence of acetic anhydride. Gentisein on methylation yielded gentisin, while gentisin on further methylation gave a mono-



(I)



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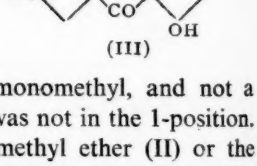


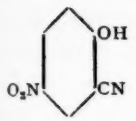
(III)

methyl ether.[5] The methylation of gentisin to a monomethyl, and not a dimethyl ether, indicated that the original methoxyl was not in the 1-position. Gentisin therefore had to be formulated as the 7-methyl ether (II) or the 3-methyl ether (III). In order to determine which of these two monomethyl ethers of gentisein was identical with gentisin, Kostanecki and Tambor[6] attempted to synthesise the 7-methyl ether by distilling a mixture of 2-hydroxy-5-methoxybenzoic acid, phloroglucinol and acetic anhydride, but they found that the product consisted of a mixture of gentisein, its dimethyl ether and a very small quantity of gentisin. This synthesis did not afford conclusive proof of the constitution of gentisin, as the possibility of its production from gentisein by methylation could not be excluded.

By a study of *dis*azobenzene-gentisin, which formed a diacetyl derivative, Perkin[7] suggested that gentisin should be the 3-methyl ether (III). If (II)

represented gentisin, the diazo coupling would have taken place in the 2:4-positions, and Perkin had found that such disazo resorcinol derivatives did not undergo acetylation under the usual conditions. It will be shown in a later communication that the diazo coupling of euxanthone and gentisin does not take place in the positions indicated by Perkin, but the constitution assigned by him to gentisin has now been confirmed by an unambiguous synthesis. Shinoda[8,9] synthesised the 7-methyl ether (II) by a Hoesch reaction between 5-methoxysalicylonitrile and phloroglucinol, followed by cyclicisation, and found that it was different from gentisin. We have synthesised the 3-methyl ether (III), which has proved to be identical with natural gentisin.

The Hoesch reaction between 5-nitrosalicylonitrile (IV) and phloroglucinol, following the method of Nishikawa and Robinson[10] for 1:3-dihydroxyxanthone, gave 7-nitro-1:3-dihydroxyxanthone (V), m.p. 295–296° (*diacetate*, m.p. 182–83°). Yumoto[11] who prepared (V) by a similar method quotes the m.p. 281–82° (*diacetate*, m.p. 162–63°). Reduction of (V) with alkaline hydrosulphite gave 7-amino-1:3-dihydroxyxanthone (VI), which on diazotisation and hydrolysis by 35% sulphuric acid yielded gentisein (I). When (V) was methylated by means of dimethyl sulphate



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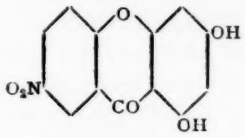

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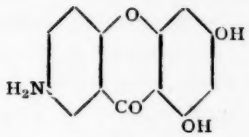
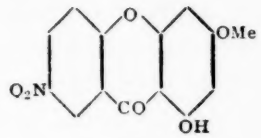
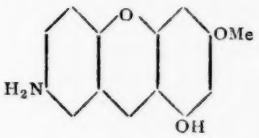


(VI)

and alkali, the ether (VII) was always contaminated with a little of the dimethyl ether, and the pure monomethyl ether was not isolable even after repeated crystallisation. It could, however, be readily obtained by methylation with diazomethane (one mol.) in ether solution. The nitro compound (VII) was then reduced to the amine (VIII) by iron and acetic acid. On



(VII)



(VIII)

diazotisation of the amine (VIII) and hydrolysis with 40% sulphuric acid, 1:7-dihydroxy-3-methoxy-xanthone, m.p. 266–67°, was obtained, identical in all its properties with natural gentisin.

Experimental

5-Nitrosalicylonitrile (IV)[13; 14]

5-Nitrosalicylaldehyde (m.p. 126°) was prepared by the nitration of salicylaldehyde,[12] and the mixture of 3-nitro- and 5-nitrosalicylaldehyde thus obtained was separated by fractional crystallisation of their sodium salts from water, in which the sodium salt of the former was more soluble. 5-Nitro-2-hydroxy-benzaldoxime, prepared in the usual manner, crystallised from alcohol in stout, colourless needles, m.p. 219°-20° (Found: N, 15·1. $C_7H_6N_2O_4$ requires N, 15·2%). 5-Nitrosalicylonitrile, obtained on treatment of the oxime with boiling acetic anhydride for 2 hours and subsequent hydrolysis of the acetate (m.p. 55–56°), either by 5% warm sodium hydroxide solution or by heating with water on the water-bath for 2–3 hours, crystallised from water in straw-yellow, long silky needles, m.p. 194–96° (Walker,[13] m.p. 194–96; Bone,[14] m.p. 190°) (Found: N, 17.2. $C_7H_4N_2O_3$ requires N, 17·1%). The nitrile dissolves in sodium bicarbonate solution with effervescence, and gives a deep red colour with ferric chloride.

7-Nitro-1 : 3-dihydroxyxanthone (V)

Through a cooled solution of 5-nitrosalicylonitrile (3·3 g.) and phloroglucinol (2·5 g.) in dry ether (150 c.c.) containing 2 g. of freshly fused zinc chloride, a slow stream of dry hydrogen chloride gas was passed for 5 hours. The oil, which first separated in about an hour, gradually dissolved, giving a deep red solution. A deep orange oil again separated after 4 hours. The mixture was left in a refrigerator for 72 hours, the ether decanted off, the deep orange viscous oil washed twice with ether, and taken up in 10 per cent. aqueous caustic soda. On boiling for an hour, when no more ammonia was evolved, the deep brownish red solution was filtered from unreacted zinc hydroxide. The 7-nitro-1 : 3-dihydroxyxanthone, obtained by acidifying the filtrate, crystallised from alcohol in light yellow, shining, flat plates (1·7 g.), m.p. 295–96° (Found: N, 5·3. $C_{13}H_7NO_6$ requires N, 5·1%). It gives a brownish violet colour with ferric chloride, and a deep red colouration when shaken with sodium amalgam in water.

Its diacetate prepared by refluxing with acetic anhydride and pyridine crystallised from alcohol in colourless needles, m.p. 182–83° (Found: N, 4·1. $C_{17}H_{11}NO_8$ requires N, 3·9%).

7-Amino-1 : 3-dihydroxyxanthone (*VI*)

7-Nitro-1 : 3-dihydroxyxanthone (0·2 g.) was dissolved in one per cent. sodium hydroxide (20 c.c.), heated to 70°, and sodium hydrosulphite added till the reduction was complete, at which stage there was a marked change

in the colour of the solution from orange to yellow. The amine, precipitated by acetic acid, crystallised as its hydrochloride from water containing hydrochloric acid in yellow needles (0·14 g.), m.p. 318°–20° (with charring) (Found: N, 4·9. $C_{13}H_{10}ClNO_4$ requires N, 5%).

1:3:7-*Trihydroxyxanthone* (*Gentisin*) (*I*)

The amine hydrochloride (0·1 g.) was dissolved in a mixture of water (10 c.c.), acetic acid (2 c.c.) and concentrated hydrochloric acid (0·2 c.c.), cooled, and diazotised, by sodium nitrite (0·03 g.). After keeping at 0–5° for 15 minutes, excess of nitrous acid was destroyed by urea, and the diazo solution slowly added in about five minutes to 30 c.c. of boiling 35 per cent. sulphuric acid. Boiling was continued for 5 minutes, when the diazo salt had completely decomposed, as tested by β-naphthol. On cooling the solution, the yellow product was ether-extracted, and the ether removed. The pinkish yellow residue crystallised from dilute alcohol in thin yellow needles (0·05 g.), m.p. 314–15° (Kostanecki and Tambor,[5] 315°). The substance dissolves in aqueous sodium hydroxide to form an orange sodium salt and a yellow solution; gives a brownish green colour with ferric chloride; and a blood-red colour when vigorously shaken with sodium amalgam in alkali.

1:3:7-*Triacetoxyxanthone*, obtained by refluxing (I) with acetic anhydride and a drop of pyridine, crystallised from acetic acid in long, thin needles, m.p. 225–26° (Kostanecki,[15] m.p. 226°).

7-*Nitro*-1-*hydroxy*-3-*methoxyxanthone* (*VII*)

7-Nitro-1:3-dihydroxyxanthone (0·27 g.) was dissolved in ether (150 c.c.) and diazomethane (0·04 g.; 1 mol.) in ether was added, and the mixture kept at the room temperature for one hour with occasional shaking, when a yellow shining mass of crystals separated. After 12 hours in the refrigerator, the product was filtered (0·23 g.). It crystallised from acetic acid—(if boiled for a long time, partial acetylation takes place)—or from benzene in light yellow, thin, rectangular plates, m.p. 249–50° (Found: N, 4·9 $C_{14}H_9NO_5$ requires N, 4·9%). The substance gives a reddish brown colour with ferric chloride. It does not dissolve in aqueous alkali, but in alcohol sodium hydroxide it gives a sparingly soluble orange sodium salt.

The *acetate* obtained by refluxing with acetic anhydride and pyridine, crystallised from acetic acid in long, thin colourless needles, m.p. 263–64° (Found: N, 4·5. $C_{16}H_{11}NO_7$ requires N, 4·2%).

7-*Amino*-1-*hydroxy*-3-*methoxyxanthone* (*VIII*)

The nitro-compound (VII; 0·2 g.) was suspended in 30 c.c. of boiling alcohol containing acetic acid (3 c.c.), and iron powder (0·2 g.) was added

to it in the course of an hour, when the nitro-compound gradually dissolved, giving a brown solution. It was refluxed for a further 30 minutes, filtered from the unreacted iron, most of the alcohol boiled off, and 2 c.c. of concentrated hydrochloric acid added, when the amine hydrochloride was precipitated. The amine crystallised as its hydrochloride from 150 c.c. of water containing hydrochloric acid, in bunches of short, thin, flat colourless needles (0·15 g.), which shrank at 270° and melted at 273–75° (with charring) (Found: N, 4·8. $C_{14}H_{12}ClNO_4$ requires N, 4·7%). The amine, liberated by neutralising the aqueous solution of the hydrochloride with sodium carbonate, crystallised from alcohol in long, thin, greenish yellow needles, m.p. 215–16° (Found: N, 5·2. $C_{14}H_{11}NO_4$ requires N, 5·4%). The alcoholic solution gives a brown colour with ferric chloride.

1 : 7-*Dihydroxy*-3-*methoxyxanthone* (*Gentisin*) (*III*)

A cooled suspension of the hydrochloride (0·15 g.) in acetic acid (4 c.c.), water (2 c.c.), and hydrochloric acid (0·2 c.c.) was diazotised by means of sodium nitrite (50 mg.). The amine hydrochloride dissolved slowly, and after keeping for 15 minutes, excess of nitrous acid was destroyed by urea, and the diazo solution added slowly to boiling 40 per cent. sulphuric acid (30 c.c.), and boiling continued for 10 minutes, when the solution gave no test for a diazo salt. On cooling and dilution, a yellow product separated which was collected, and crystallised from alcohol. The long, light yellow, shining needles (0·09 g.), softened slightly at 258–59° and melted at 266–67°, being identical in behaviour with a sample of natural gentisin. A mixture of the synthetic substance and gentisin gave the same melting point (Found: C, 65·1,; H, 3·6. $C_{14}H_{10}O_5$ requires C, 65·1, H, 3·9%). The substance exhibits all the properties described for natural gentisin. It dissolves readily in alkali with a golden yellow colour, and gives an olive-green colour with ferric chloride. When heated and shaken with sodium amalgam in water, it gives a deep green solution, which on acidification gives a cherry red precipitate. In concentrated sulphuric acid it gives a yellow solution, which on standing develops a bright green fluorescence, which earlier workers have not recorded. We have found, however, that natural gentisin behaves similarly.

The *diacetate*, obtained in the usual manner by treatment with acetic anhydride and pyridine, crystallised from alcohol in long thin needles, m.p. 195–96°, not depressed when mixed with the diacetate prepared from natural gentisin (Hlaiswetz and Habermann,[3] m.p. 195–6°).

The *dibenzoate* obtained by shaking a solution of the compound in 10 per cent. sodium hydroxide with 6–8 mols. of benzoyl chloride,

crystallised from alcohol in bunches of short thick needles, m.p. 192° (Kostanecki and Tambor,[4] m.p. 192°).

Summary

1 : 7-Dihydroxy-3-methoxyxanthone has been synthesised and shown to be identical with natural gentisin. 7-Nitro-1 : 3-dihydroxyxanthone, obtained by a Hoesch reaction between 5-nitrosalicylonitrile and phloroglucinol, followed by hydrolysis and cyclicisation, was methylated by diazomethane to its 3-methyl ether. This, on reduction, diazotisation, and hydrolysis with sulphuric acid, gave 3-methoxy-1 : 7-dihydroxyxanthone, identical in all its properties with natural gentisin.

We are greatly indebted to Dr. A. T. Peters of the University of Leeds for a sample of natural gentisin isolated by Professor A. G. Perkin.

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NUCLEAR OXIDATION IN THE FLAVONE SERIES

Part IV. New Synthesis of Herbacetin and Hibiscetin

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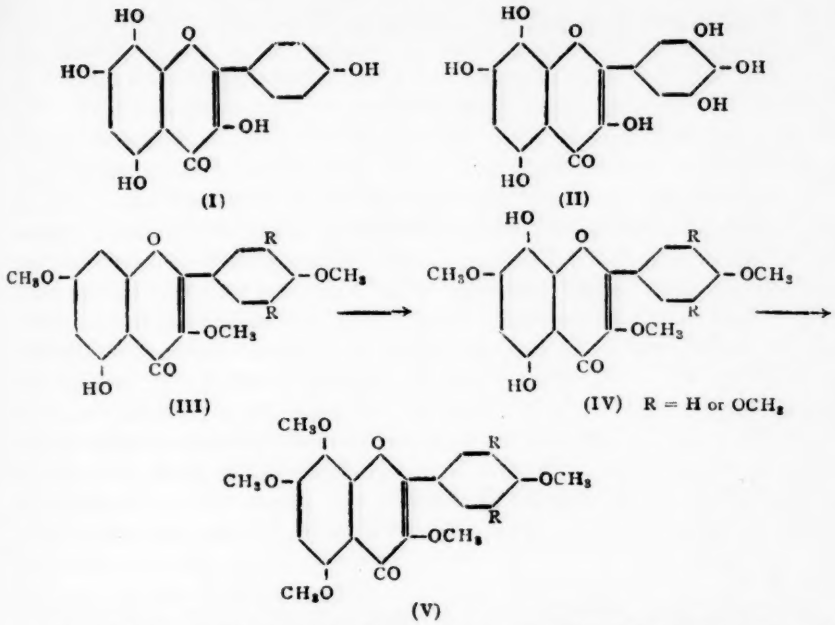
In Part I[1] was described the synthesis of gossypetin and 8-hydroxy-galangin by the nuclear oxidation of quercetin and galangin derivatives. Herbacetin (I) and Hibiscetin (II) are the other two members of this flavonol series with the 5:7:8-arrangement of hydroxyl groups. The former was first isolated by Neelakantam and Seshadri[2] from the flowers of Gossypium herbaceum and was later found to occur in the flowers of *Thespasia populnea*[3] also. Its partial methyl ether, tambulin is present in the fruits of *Zanthoxylum acanthopodium*.[4] It was first synthesised by Goldsworthy and Robinson[5] using 2:4-hydroxy-ω:3:6-trimethoxyacetophenone as the important intermediate. Hibiscetin occurs as the main component of the flowers of *Hibiscus sabdariffa*[6]; it has been synthesised by Rao, Rao and Seshadri[6] employing the above mentioned ketone.

These two flavonols have now been prepared synthetically in good yields by means of the new method of nuclear oxidation in the 8-position. Kæmpferol obtained from the flowers of *Thespasia populnea* and myricetin from the flowers of *Hibiscus cannabinus* have been employed for this purpose. As in the previous cases these were first methylated partially leaving the hydroxyl in the 5-position alone free and subsequently subjected to oxidation with persulphate. A synthetic sample of 3:3′:4′:5′-O-tetramethyl-myricetin[7] having free hydroxyls in the 5 and 7 positions has also been used. The 5:7:8-trihydroxy compound obtained in this case is only pale yellow in colour whereas the lower analogues are deeper. Such weakening of colour with increase in the number of methoxyls in the side phenyl nucleus has been noted in other cases also.[8] The reactions of the 5:8-dihydroxy and 5:7:8-trihydroxy-compounds are quite similar to those of the analogous compounds described in Part I.

3:7:4′-O-trimethyl herbacetin (IV, R= H) has also been prepared by the oxidation of herbacetin pentamethyl ether (V, R =H) with nitric acid and the reduction of the quinone thus produced.



The above synthesis establishes the biogenetic relationship between herbacetin and kæmpferol and between hibiscetin and myricetin. The first two have been found to occur together in the Indian cotton flowers and in the flowers of *Thespasia populnea*. Though myricetin has not been definitely detected in the flowers of *Hibiscus sabdriffa* which contain hibiscetin, it occurs as the main component of the flowers of the closely allied species, *H. cannabinus*.

Experimental

For the preparation of the required partial methyl ether (III), kæmpferol or myricetin was boiled in dry acetone solution with the correct quantity of dimethyl sulphate (3 or 5 mols.; a very small excess is better) and excess of anhydrous potassium carbonate for six hours. Distillation of the solvent and addition of water yielded the crude product. It was purified by conversion into the potassium salt and regeneration. Kæmpferol-trimethyl-ether melted at 152–53° and myricetin penta-methyl ether at 138–39° as reported in the literature.[9]

3:7:4′-*Trimethoxy*-5:8-*dihydroxy-flavone* (IV, R= H)

(*a*) *By oxidation with persulphate.*—A solution of 3:7:4′-trimethoxy-5-hydroxy-flavone (III, R = H) (0·6 g.) in a mixture of pyridine (15 c.c.)

and aqueous potassium hydroxide (0·6 g. in 40 c.c.) was vigorously stirred and treated dropwise with an aqueous solution of potassium persulphate (0·8 g. in 50 c.c.) during the course of 2 hours. The deep green solution was kept for 24 hours and then rendered slightly acidic to Congo Red. The brown solid that separated out was filtered off and the filtrate extracted twice with ether (20 c.c. each time). The clear brown solution was treated with sodium sulphite (2 g.) and concentrated hydrochloric acid (20 c.c.) and kept in a boiling water-bath for 30 minutes during which time a yellowish brown crystalline solid separated out. It was filtered off after cooling the solution and washed free from acid. On extracting the filtrate with ether a little more was obtained. Yield 0·3 g. Crystallisation from alcohol yielded shining yellow rectangular plates and prisms melting at 196–98° (Found: C, 62·8; H, 4·4; $C_{18}H_{16}O_7$ requires C, 62·8; H, 4·7%). It was sparingly soluble in alcohol and ethyl acetate. In 5% aqueous sodium hydroxide it readily dissolved to a deep red solution which turned to bluish violet in a few minutes. It gave with ferric chloride in alcoholic solution a green colour which changed to brown. With *p*-benzoquinone in alcoholic solution a deep red colour was obtained with the gradual deposition of a red crystalline solid.

The dihydroxy compound (IV) (0·1 g.) was dissolved in dry acetone (25 c.c.) and treated with dimethyl sulphate (0·5 c.c.) and anhydrous potassium carbonate (5 g.). After refluxing for 6 hours the solvent was distilled off and the residue treated with water. The methyl ether was filtered and crystallised from alcohol when it came out in the form of colourless narrow rectangular plates melting at 154–56° alone or in admixture with an authentic sample of the pentamethyl ether of herbacetin.

(*b*) *By demethylation with nitric acid.*—Nitric acid (4 c.c.; d, 1·25) was added to herbacetin-pentamethyl-ether (V, R= H, 0·2 g.) with vigorous stirring while keeping the temperature below 15°. The substance dissolved to a yellow solution which soon changed to orange and finally deep red. A deep red product separated which soon solidified in a few minutes. It was filtered off and washed with nitric acid (d, 1·25) followed by water. Crystallisation from alcohol yielded deep red spear shaped crystals melting at 220–22°. It was sparingly soluble in alcohol. It readily dissolved in aqueous sodium hydroxide to an intense bluish violet solution. When a solution of the substance in acetic acid was treated with aqueous sodium sulphite a bright yellow solid separated which on crystallisation from alcohol came out in the form of yellow rectangular plates melting at 196–98° identical with the dihydroxy compound (IV, R= H) obtained by the oxidation of 5-hydroxy-3 : 7 : 4′-trimethoxy-flavone (III).

5: 8-*Dihydroxy*-3: 7: 3′: 4′: 5′-*pentamethoxy-flavone* (IV, R= OCH_3)

To a stirred solution of 3: 7: 3′: 4′: 5′-O-pentamethyl myricetin (III, R = OCH_3) (1 g.) in a mixture of pyridine (20 c.c.) and aqueous potassium hydroxide (0.75 g. in 25 c.c.) was added dropwise a solution of potassium persulphate (1 g. in 50 c.c.) during the course of 2 hours. The colour of the solution first changed to intense olive green and then gradually to deep brown. After keeping it for 24 hours it was just acidified, the pale brown solid that separated out was filtered and the filtrate extracted with ether twice. The clear brown aqueous layer was then treated with sodium sulphite (2 g.) and concentrated hydrochloric acid (25 c.c.) and kept in the boiling water bath for 30 minutes. The yellowish brown solid that separated out was filtered off and washed well; the filtrate on ether extraction yielded some more of the product. Yield 0.5 g. It was crystallised twice from alcohol from which it came out in the form of lustrous golden yellow long rectangular prisms and rods melting at 200–202°. (Found: C, 59.7; H, 4.6; $C_{20}H_{20}O_9$ requires C, 59.4; H, 5.0%). It was readily soluble in aqueous sodium hydroxide to a deep red coloured solution which changed to bluish violet in a few minutes. In alcoholic solution it gave with ferric chloride a transient green colour which changed to brown. With *p*-benzoquinone a reddish brown colour was obtained together with the slow deposition of a red solid.

The dihydroxy compound (0.2 g.) was methylated by boiling for 6 hours with dry acetone (25 c.c.), dimethyl sulphate (0.5 c.c.) and anhydrous potassium carbonate (5 g.). When crystallised from alcohol the methyl ether separated in the form of colourless rectangular plates melting at 192–93°. Mixed melting point with an authentic sample of hibiscetin-hepta-methyl-ether (V, R= OCH_3) was not depressed.

5: 7: 8-*Trihydroxy*-3: 3′: 4′: 5′-*tetramethoxy-flavone*

A stirred solution of 3: 3′: 4′: 5′-tetramethyl ether of myricetin[7] (1 g.) in aqueous potassium hydroxide (1 g. in 30 c.c.) was treated with potassium persulphate solution (1 g. in 50 c.c.) drop by drop for 2 hours. The deep brown solution was kept for 24 hours and neutralised. The brown solid precipitate was filtered off and the filtrate extracted with ether twice. The aqueous solution was treated with sodium sulphite (2 g.) and concentrated hydrochloric acid (25 c.c.) and kept in a boiling water bath for 30 minutes. The glistening brown crystalline solid that separated out was filtered and washed. The filtrate yielded some of the substance on extraction with ether. Yield 0.55 g. Crystallisation from alcohol and subsequently from ethyl acetate yielded pale yellow short rectangular plates and prisms melting at 257–58° (Found: C, 58.3; H, 4.3; $C_{19}H_{18}O_9$ requires C, 58.5; H,

4.6%). It was very sparingly soluble in ethyl acetate. With ferric chloride in alcholic solution it gave a deep greenish brown colour. In 5% sodium hydroxide it dissolved quickly to form a deep brown red solution wich soon faded to a pale blue colour. In 5% sodium carbonate it dissolved to a brown solution wich changed to pale greenish yellow.

Methylation of the trihydroxy compound (0.1 g.) in anhydrous acetone medium (20 c.c.) with dimethyl sulphate (0.5 c.c.) and potassium carbonate (5 g.) yielded the heptametyhl ether which crystallised from alcohol in the form of colourless rectangular plates melting at 192–93° identical with the heptamethyl ether of hibiscetin (V, R= OCH_3).

Summary

The synthesis of herbacetin and hibiscetin from kæmpferol and myricetin is described. As before, the partial methyl ethers of the latter have been subjected to nuclear oxidation with alkaline persulphate. The oxidation proceeds smoothly and gives rise to good yields of the products.

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COLOURING MATTER OF TAMBUL SEEDS

Part I. Tambuletin

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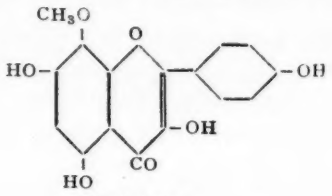
The new flavonol herbacetin was first isolated from the Indian cotton flowers.[1] In these it occurs along with gossypetin, quercetin and also kæmpferol (populnetin). Later it was found to be present in the flowers of *Thespasia populnea* along with kæmpferol.[2] Its isolation from these sources is difficult since it involves fractionation and separation of mixtures and since the flowers vary very markedly in composition. The discovery by Bose and Bose[3] of tambulin, a trimethyl ether of herbacetin in the fruits of *Zanthoxylum acanthopodium* (tambul seeds) unaccompanied by any other flavonol seemed to suggest that this may prove to be a convenient source of natural herbacetin when required in small quantities. We had occasion to examine these seeds with this object in view.

The seeds were obtained from Calcutta and when extracted by the original method of the above authors using boiling alcohol or by an improved method using cold acetone surprisingly did not yield tambulin, but gave another crystalline compound which we have now named tambuletin, the yield being about 0·03%. A number of samples were procured and extracted at different times during the past two years and the same results were repeated.

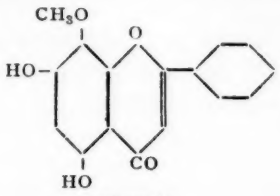
Bose and Bose[3] reported that tambulin melted at 205° and formed an acetate melting at 160–61°. It had the composition $C_{18}H_{16}O_7$ and had three methoxyl groups in the molecule. On further methylation it yielded the pentamethyl ether of herbacetin. Tambuletin on the other hand is now found to melt at 269–71° and to yield an acetate melting at 140–42°. Its composition is represented by the formula $C_{16}H_{12}O_7$ and it has only one methoxyl. However like tambulin it yields O-pentamethyl herbacetin on complete methylation. Further on demethylation herbacetin itself is obtained. Consequently it should be considered to be a monomethyl ether of herbacetin and thus the tambul seeds could be used as a handy source of natural herbacetin.

The properties and colour reactions of tambuletin provide some information about the location of the methyl ether group. They resemble closely those of kæmpferol. Particularly significant are (1) the ferric chloride colour, (2) colour in sodium hydroxide solution and (3) lack of reaction

with *p*-benzoquinone. These indicate that one of the two hydroxyl groups in the 5- and 8-positions is not free. Since the 5-hydroxyl is difficult to methylate and will be the last one to be affected in hydroxy flavones, it could be concluded that the methoxyl is situated in the 8-position and that tambuletin is another example of the rare type of 8-methyl ethers analogous to wogonin. Work is in progress in order to confirm this constitution.



Tambuletin



Wogonin

Bose and Bose reported the isolation in a very small yield of a second substance named tambulol melting at 265–67°. Though its melting point is very near that of tambuletin its composition and properties are very different.

Experimental

Isolation of Tambuletin:

For the extraction of the fruits of *Zanthoxylum acanthopodium* Bose and Bose[3] employed hot rectified spirit. Cold acetone is now found to be better. The fruits (3 kg.) were crushed to a coarse powder and extracted with acetone by cold percolation. Each time the solvent was allowed to be in contact with the material for 24 hours and the extract drained off; this was repeated three times. The solvent was distilled off as far as possible on a water-bath and the concentrated extract (600 c.c.) was thoroughly mixed with petroleum ether (2 litres). It was set aside for a fortnight when a bright yellow solid along with some brown resin separated out. The supernatant layer of petroleum ether (A) was filtered off and the residue stirred up with a little cold alcohol and filtered. A yellow solid was thus obtained and this was washed free from the accompanying resinous material with a little more alcohol. The alcohol solution was marked (B). The yellow substance melted at 254–56°. Taking advantage of the fact that it dissolves freely in aqueous sodium hydroxide and can be recovered unchanged by acidifying the solution, the crude material was purified in the following manner. It was dissolved in aqueous alkali and the solution was quickly filtered thus removing all suspended impurities. The clear solution was acidified with hydrochloric acid and the precipitated solid was recovered by filtration; ether extraction of the aqueous filtrate did not yield any more of it. It was further purified by crystallisation from glacial acetic

acid when it was obtained as bright yellow needles melting at 269–71°. Even without the alkali treatment the crude material could be purified by repeated crystallisation from glacial acetic acid to give the above melting point (Found: C, 60·4; H, 4·0; OCH_3, 9·4; $C_{16}H_{12}O_7$ requires C, 60·7; H, 3·8; OCH_3 9·8%).

The petroleum ether extract (A) was examined for the existence of any crystalline matter. When the solvent was distilled off, there remained a very small quantity of a brown sticky solid. This was extracted with aqueous alkali and the solution acidified. The same coloured and sticky substance was obtained and all attempts to get a crystalline substance from it using different solvents failed.

Similarly the alcohol washings (B) also were examined. The solvent was removed by distillation and the residue was obtained as a brown pasty mass. When it was shaken with petroleum ether, some more tambuletin was precipitated. From the remaining amorphous portion no other crystalline substance could be obtained even after repeated effort.

Thus only tambuletin melting at 269–71° could be isolated from the total acetone extract and the presence of no other crystalline compound could be detected.

Tambuletin is a bright yellow solid which is readily soluble in hot glacial acetic acid but more sparingly in hot ethyl acetate, acetone and alcohol. When its alcoholic solution is treated with concentrated hydrochloric acid and magnesium powder the solution which is initially coloured bright yellow turns bright orange-red. With ferric chloride in alcoholic solution it gives a dull green colour and this colour is stable and does not change to brown with excess of the reagent. When an alcoholic solution of the substance is treated with neutral lead acetate in the same solvent an orange coloured precipitate is thrown down. With concentrated sulphuric acid the crystals of the substance immediately develop a bright red colour and go into solution later; the solution is coloured brownish-yellow and does not exhibit any fluorescence. Tambuletin dissolves easily in aqueous alkali to form a bright yellow solution; the colour of the alkali solution is stable for 12 hours and the substance could be recovered by acidification after this period. In absolute alcoholic solution tambuletin does not react with *p*-benzoquinone.

Methyl tambuletin

Tambuletin (0·2 g.) was dissolved in dry acetone (50 c.c.) and anhydrous potassium carbonate (5 g.) and dimethyl sulphate (0·5 c.c.) were added. The contents were refluxed for 30 hours and the hot acetone solution filtered

from the potassium salts which were finally washed with hot acetone. On distilling the combined acetone solution to remove the solvent, the crude methyl ether was obtained. It was crystallised twice from dry ethyl acetate when it melted at 156–57°. The mixed melting point with herbacetin-penta-methyl-ether was undepressed.

Nor-tambuletin

Tambuletin (0·5 g.) was dissolved in hot acetic anhydride (1 c.c.) and the solution cooled. To this was added hydriodic acid (d., 1·7; 5 c.c.) with cooling under the tap. The contents were boiled for one hour, cooled and treated with water containing sulphur dioxide. The precipitated yellow solid was filtered off and crystallised from dry ethyl acetate when it was obtained as bright yellow flat needles melting at 279–80°. The mixed melting point with herbacetin was undepressed. The identity was established by comparing the reactions of nortambuletin and herbacetin (1) with alkaline buffer solutions, (2) with *p*-benzoquinone and (3) with ferric chloride. Both gave identical colour changes with (1), the brownish-red quinone with (2) and with (3) the colour was olive green changing to reddish-brown with excess of the reagent.

Acetyl-tambuletin

Tambuletin (0·5 g.) was treated with acetic anhydride (10 c.c.) and a few drops of pyridine. The contents were refluxed gently for one hour and poured into ice-cold water. The reaction mixture was stirred well and set aside for some time. The separated solid was filtered off, dried and crystallised from dry ethyl acetate when it was obtained in the form of colourless needles melting at 140–42°.

Summary

Extraction of the fruits of *Zanthoxylum acanthopodium* has yielded a new crystalline component and it is named tambuletin. It seems to occur in the place of tambulin reported by earlier workers. It has the composition $C_{16}H_{12}O_7$ and is a monometyl ether. Experiments on methylation and demethylation prove that it is a monomethyl ether of herbacetin and its reactions suggest that the methoxyl group is in the 8-position.

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LOCALISATION OF THE DISCHARGE TUBES PART II

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1§. In a previous paper[1] were reported the results obtained during the course of a quantitative study of the well-known phenomenon of the localisation of the discharge current on the cathode surface, in the case of a normal D.C. discharge, both as a function of the gas in the discharge tube and of the length of the cathode dark space or of the discharge voltage. The object of the present paper is to report the results of further experiments carried out with neon, with a discharge tube 3·5 cm. in diameter and with hydrogen and air in the case of a discharge tube of a smaller diameter, *viz.*, 2·5 cm. The localisation effect has been generally ascribed to the space charge developed on the walls of the discharge tube near the cathode. It would follow as a consequence of the above hypothesis, that it would be influenced to a great extent by the size of the discharge tube. On general ground, one may as a matter of fact, expect to find a more pronounced localisation in the case of narrow discharge tubes. The observations reported in this paper were undertaken, to study this aspect of the problem experimentally.

2§. The experimental arrangement used for the first part of the investigation, consists of a discharge tube 3·5 cm. in diameter provided with an aluminium anode and a composite cathode consisting of three sectors of moulded aluminium which are insulated from each other by thin rings of ebonite material. The first sector extends from the centre to 0·40 cm. and has an area of 0·50 cm.^{2} The second covers a region lying between 0·50 cm. and 0·95 cm. from the centre with a total area of 2·05 cm.^{2} The third covers a region between 1·10 cm. to 1·55 cm. with an area of 3·74 cm.^{2} The three sectors of the cathode are separately earthed through three different milliammeters. The H.T. used is obtained from a transformer coupled with a rectifying Kenetron circuit, the anode being connected to the H.T. The pressure of the gas in the tube is very roughly between 0·4 to 0·00015 cm. Hg. Table I gives the results obtained for neon. Here M_1, M_2, M_3, M, represent as before the current received by the first, second, third sector and the total cathodic current respectively, A_1, A_2 and A_3 are the corresponding

TABLE I

Ordinary discharge in neon. Diameter of the discharge tube 3·5 *cm. Total current* 1·6 *m.a.*

D.S.L. cm.	H. T. volts	M_1/MA_1	M_2/MA_2	M_3/MA_3
0·5	450	0·18	0·15	0·16
1·0	650	0·18	0·18	0·14
1·5	..	0·24	0·24	0·10
2·0	..	0·38	0·29	0·06
2·5	..	0·50	0·31	0·03
3·0	2100	0·80	0·27	0·01
3·5	2800	0·94	0·24	0·01
4·0	5000	1·31	0·15	0·01

areas of the three sectors respectively. D.S.L. represents the length of the cathode dark space.

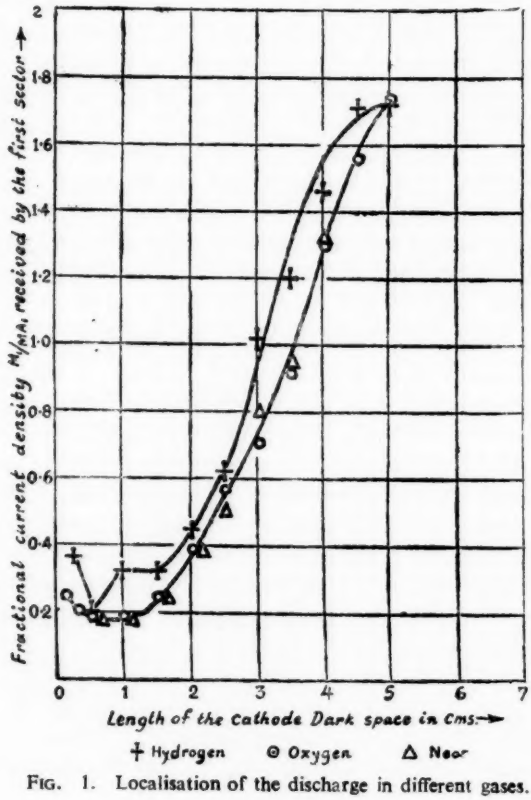

FIG. 1. Localisation of the discharge in different gases.

Comparing these results with those given for hydrogen and air in Tables V and VII of the previous paper [which will be referred to as (I) in what follows] we observe that the values obtained for neon are practically the same as those obtained for hydrogen and air. The values obtained for hydrogen under the same conditions are, however, slightly higher than those obtained for neon and air. This is well shown by Fig. 1 which gives the fractional current received by the first sector, as a function of the length of the cathode dark space in the case of hydrogen, air and neon. Apart from these slight differences, the results in general confirm what had already been observed in (I), that the localisation does not show any appreciable dependence on the nature of the gas in the discharge tube.

3§. For the second part of the experiments, the experimental arrangement and the mode of observation remain the same. The discharge tube now used however, has a diameter of 2·5 cm. The three sectors of the cathode extend from 0–0·40 cm., 0·5–0·80 cm., 0·9–1·25 cm., respectively with areas of 0·50, 1·226, and 2·364 cm.^{2} The sectors are insulated from each other by rings of ebonite, and are then connected to earth, through three separate milliammeters. Table II shows the observations obtained for ordinary discharge in hydrogen. The results have been expressed in the first instance, in terms of the average current densities.

TABLE II

Ordinary discharge in hydrogen. Diameter of the discharge tube 2·5 *cm. Total current* 1·6 *m.a.*

D.S.L. cm.	H. T. volts	M_1/A_1	M_2/A_2	M_3/A_3
0·2	550	0·60	0·51	0·27
0·5	..	0·50	0·49	0·31
1·0	700	0·70	0·69	0·17
1·5	..	1·00	0·81	0·05
2·0	..	1·50	0·65	0·02
2·5	2700	2·40	0·25	0·01
3·0	3300	2·90	0·12	0·01
3·5	4200	3·00	0·08	0·01

From these observations, it will be seen that under the conditions studied here, there is a concentration of the current in the centre shown by the fact that the current density has got its highest value on the first sector except in the case of a few observations for small values of the D.S.L. This effect is specially marked for high values of the D.S.L., whereas for low values the average magnitude of the current density appears to be the same for the area covered by the first two sectors. As a result of the observations obtained in (I), the empirical relation $e^{-h^2r^2}$ was proposed to represent the

radial distribution of the current density on the cathode surface where h was a variable depending on the value of the D.S.L. When values of h were calculated for the observations given above, it was found that the expression holds good only for large values of the D.S.L. This is shown by the following table which gives both the experimental and the theoretically calculated values for M_1/M, M_2/M, M_3/M, side by side, with the appropriate values of h shown in the last column. Table IV shows the observations in the case of air.

TABLE III

Ordinary discharge in hydrogen. Diameter of the discharge tube=2·5 *cm. Total current* 1·6 *m.a.*

D.S.L. cm.	M_1/M Expt.	M_1/M Theor.	M_2/M Expt.	M_2/M Theor.	M_3/M Expt.	M_3/M Theor.	h
0·5	0·15	0·15	0·37	0·36	0·47	0·48	0·50
1·0	0·22	0·22	0·53	0·41	0·25	0·37	0·95
1·5	0·31	0·34	0·62	0·51	0·06	0·15	1·40
2·0	0·47	0·48	0·50	0·42	0·03	0·10	1·80
2·5	0·78	0·77	0·20	0·23	0·02	0·01	2·70
3·0	0·90	0·90	0·09	0·09	0·02	0·00	3·46
3·5	0·94	0·44	0·06	0·06	0·00	0·00	3·70

TABLE IV

Ordinary discharge in air. Diameter of the discharge tube=2·5 *cm. Total current* 1·6 *m.a.*

D.S.L. cm.	H. T. Volts	M_1/M	M_2/M	M_3/M	M_1/A_1	M_2/A_2	M_3/A_3
					m.a. per sq. cm.		
0·2	..	0·12	0·53	0·34	0·24	0·43	0·14
0·5	..	0·12	0·53	0·34	0·24	0·43	0·14
1·0	..	0·22	0·56	0·22	0·44	0·45	0·09
1·5	..	0·31	0·65	0·03	0·62	0·53	0·01
2·0	..	0·51	0·47	0·01	1·02	0·38	0·00
2·5	3500	0·75	0·22	0·01	1·50	0·17	0·00
3·0	4400	0·88	0·10	0·01	1·76	0·08	0·00
3·5	5800	0·94	0·06	0·00	1·98	0·05	0·00

4§. Compared with the variation of h obtained in (I) which was from 1·99 to 3·386, the present results show a more pronounced change. The lowest value of h is 0·50 and the highest 3·70, which means that the localisation effects are less marked at small values of the D.S.L. but develop more rapidly with increasing D.S.L. and reach a comparatively higher magnitude

than what was found in the previous case. For the observations obtained for low values of the D.S.L., the empirical expression previously suggested, does not appear to hold good. An expression of the type $e^{-h^2(r-r_0)^2}$ with appropriate values for h and r_0 seems to answer better. Such an expression for the current density would indicate that the discharge beam coming towards the cathode is in the form of a ring. There are two observations which perhaps may be taken to indicate such a possibility. In Table IV which shows the values obtained in the case of air, one observes that the current density for the first three observations, is greater on the second sector than on the first. On looking up the results reported in (I), I find one observation, also obtained for air, which brings out the same fact [Table IX, page 448 of (I)]. The current density on the first sector in this case is 0·272 as compared with 0·396 on the second sector. One may not finally conclude from these results that the discharge beam has a ring structure for low values of the D.S.L. because only the observations for air seem to support it in a conclusive and direct manner, whereas such a result is not obtained in the case of hydrogen. However one observes from the values given in Table II even for hydrogen, that the current density in the case of both the first and the second sector starts with a high value as the D.S.L. is increased, reaches a minimum value, after which point the behaviour of the current density on the two sectors is different. In the case of the first sector, it increases rapidly with the D.S.L., whereas the current density on the second, reaches a maximum value of 0·81 ma./cm.^{2} for D.S.L.= 1·5 cm., and then decreases for values greater than this. The current density on the third sector starts with a low value, reaches a maximum of 0·31 ma./cm.^{2} for D.S.L.= 0·5 cm., and then falls off rapidly for higher values of the same. Although the maximum value of the current density observed on the third sector is less than that observed on the second, which is in turn less than that obtained on the first, nevertheless the results indicate that in the beginning, there is a redistribution of the current on the cathode surface, with a general movement away from the centre towards the periphery of the cathode (which may or may not mean an actual shift of the maximum of the current density from the centre of the cathode) followed by a rapid concentration of current towards the centre as the D.S.L. increases. The results obtained in the case of both air and hydrogen, again show the definite failure of proposed empirical relation for low D.S.L. From the results obtained for the average current densities, one can see that the curve representing the radial distribution of the current should have a broader maximum at the centre (shown by the fact that the current density has got almost the same value for the first two sectors for small D.S.L.)—assuming that the

maximum always obtains at the centre—followed by a much more rapid fall than is given by the above expression. The expression proposed on the other hand explains very well the observations obtained for high values of the D.S.L. There is thus a change in the form of the radial distribution of the current as one increases the D.S.L. We observe therefore that the size of the cathode affects the localisation in two ways in the case of the narrow tubes (1) the magnitude of the localisation is greater than that obtained for wide tubes, (2) the form of the radial distribution of the current density on the cathode surface is changed for low values of the D.S.L., for higher values the form is the same in the case of both narrow and wide discharge tubes. One may expect to find therefore corresponding effects on the canal ray beam formation in the case of the two types of canal ray discharge tubes.

In the end I offer my grateful thanks to Prof. Dr. S. S. Joshi for giving me the facilities for work and constant encouragement. I am indebted to Prof. Dr. R. K. Asundi for advice and useful discussions. I have to thank Dr. D. V. Gogate, Head of the Physics Department, Baroda College, for useful discussions.

Summary

The phenomenon of the localisation of the discharge in ordinary discharge tubes has been studied quantitatively as a function of the gas in the discharge tube and of the size of the tube. The nature of the gas is found to have very little influence on the localisation. The size of the discharge tube, on the other hand, is found to exert an appreciable influence. In the case of narrow tubes, the magnitude of the localisation is greater and secondly for low values of the D.S.L. the form of the radial distribution of the current density on the cathode surface is modified to a great extent. For high values of the D.S.L. the empirical expression previously proposed is found to hold good.

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FARADAY EFFECT IN SOME CUBIC CRYSTALS

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1. Introduction

It is well known that the magnitude of the Faraday rotation in solids or liquids is generally less than that given by the celebrated Becquerel formula which connects it with the optical dispersive power. The percentage ratio of the observed magnetic rotation to that theoretically predicted is called the magneto-optic anomaly. An examination of the available data, especially those obtained in some recent studies by the author (1946) indicate that the magneto-optic anomaly is related to the nature of the electronic binding between the atoms in the solid. In particular, a comparison of the Faraday rotations in diamond and in zinc-blende (Ramaseshan, 1946) disclosed the remarkable result that in spite of the apparent similarity in their structures, the magneto-optic anomaly for diamond is only 28% while that in zinc-blende is 91%. This suggested that the determination of the magneto-optic anomaly of a series of crystals of simple constitution and structure might succeed in giving an insight into the state of the electron atmosphere in crystals. With this object in view, the present investigation was undertaken. It describes measurements made with five cubic crystals, *viz.*, LiF, NH_4Cl, KBr, NH_4Br and MgO for which no record of Faraday effect measurements could be traced in the literature. As a check on the accuracy of the work, measurements have also been made with three crystals, NaCl, KCl and CaF_2, for which data are already available.

2. Materials Studied

In the determination of the Verdet constant, it is absolutely essential that the crystal to be used should have no residual birefringence. Birefringence induced by strain is known to affect Faraday effect measurements in two ways. Firstly, the restoration of light due to birefringence when the crystal is observed between crossed nicols makes it difficult to observe the restoration produced by the magnetic field. Consequently, the accurate determination of the extinction position becomes difficult. Secondly, the Faraday effect in isotropic substances is known to diminish in the presence of small amounts of birefringence. However, all the crystals

excepting those of MgO and NH_4Br used in the present investigation were free from this defect.

A large crystal of lithium fluoride of size approximately $3\times 2\times 2$ cm., purchased from Harshaw Chemical Co., Ltd., U.S.A., was employed. All its faces were well polished and it proved ideal for Faraday effect measurements. Five crystals of synthetic periclase presented to Sir C. V. Raman by Messrs. Norton & Co., Worcester, U.S.A., were found suitable for the measurement of the Verdet constant in MgO. All the crystals had a small amount of residual birefringence but in four of them this was so small that it did not affect the measurements. Two fine crystals of fluorspar with polished faces, one colourless and the other showing a violet fluorescence, which were originally in possession of Fizeau and now form part of Sir C. V. Raman's crystallographic collection, were available for these studies. Large clear cleavage plates of rocksalt from Baluchistan were used. The ammonium chloride and bromide crystals were grown by Mr. K. G. Ramanathan in this laboratory for some spectroscopic studies. The crystals were $1\times 1\times 0{\cdot}5$ cm. in size. The potassium bromide and chloride crystals were grown by the author by the method of slow evaporation of a saturated solution.

3. Experimental Procedure

The Verdet constant V of a substance can be expressed by the modified Becquerel formula

$$V=\gamma\,(e/2mc^2)\,\lambda dn/d\lambda,$$

where e and m are the electronic charge and mass respectively, λ and c the wavelength and velocity of light and n is the refractive index of the substance. The factor γ in many substances remains constant over the visible and the near ultraviolet provided the dispersion due to the infra-red terms is eliminated from the formula (Darwin and Watson, 1927). To calculate the value of $\lambda dn/d\lambda$ of a substance, fairly accurate measurements of the refractive indices for a few wavelengths in the visible region are necessary.

The refractive indices of these crystals were determined with the aid of a Pulfrich refractometer made by Carl Zeiss & Co. As most crystals had the form of rectangular parallelepipeds with polished faces, there was not much difficulty in the measurements. Monobromonaphthalene, methylene iodide and a solution of sulphur in methylene iodide were the liquids used to cement the solids to the Pulfrich prism. The refractive indices were determined for the wavelengths λ 5893, λ 5461 and λ 4358. The refractive index measurements were accurate to one unit in the fourth place of decimals for MgO, NH_4Cl, NH_4Br and KBr and to two units in

the fifth place for LiF. The dispersion is accurate to 1% or 2%. The dispersion of fluorspar has been determined from the values of refractive indices given in Landolt and Bornstein tables.

An electromagnet of the Rutherford type with its polepieces 28 mm. apart was used. In the earlier determination with LiF the polepieces were kept 32 mm. apart, but later this was reduced to 28 mm. A sodium lamp and a mercury pointolite lamp with suitable filters were used as the sources of light. A wide-angle nicol was used to polarise the light. The magnetic rotation of the light was determined by means of a Laurents polarimeter consisting of a sugar half-shade and a small analysing nicol. The sugar half-shade (Rayleigh, 1884) consists of a cell containing sugar solution arranged such that the two halves of the cell in the field of view are subjected to small rotations, differing by about 2°. The difference in the thickness in the path is obtained by introducing a piece of unstrained glass inside the cell such that the upper edge of the glass divides the field of view into two parts. With this half-shade it is possible to determine the position of equal intensity within 1′ or 2′ of arc. In each measurement the position of equal intensity was determined first without the magnetic field and then with the field on and reversed. A mean of twenty readings was usually taken. The accuracy of measurement was between ½% and 1%. It must be mentioned here that the half-shade could only be used in the case of crystals without any trace of birefringence. It was used for the measurement of the magnetic rotation in LiF, KBr, NH_4Cl, CaF_2, NaCl and KCl. For NH_4Br and MgO which had small amounts of birefringence, the half-shade was dispensed with and the approximate extinction position was determined with the aid of the analyser.

The effective field used was determined by measuring the rotation produced in conductivity water. The Verdet constant for water for λ 5893 at 25° was taken to be 0·01307 min. per cm. per gauss. The temperature at which the measurements were taken was always between 23·5° C. and 26° C.

Table I gives the rotation observed for λ 5893, λ 5461 and λ 4358 with water columns of different thicknesses. Table II to IX give the optical and magneto-optic constants of NaCl, KCl, CaF_2, LiF, KBr, NH_4Cl, NH_4Br and MgO. In these tables, n is the refractive index, ρ the actual rotation due to the magnetic field, V the Verdet constant and γ the magneto-optic anomaly.

The values obtained for KCl and NaCl agree closely with those obtained by Becquerel (1885) and Landau (1908). These values are about 5% higher than those obtained by Mayer (1909). The Verdet constant of

CaF_2 agrees closely with the values obtained by different workers (1908, 1909, 1885). The magnetic rotation for λ 4358 could not be determined

TABLE I

V_{5893} for water = 0·1307′ per cm. per gauss

Distance between polepieces in mm.	Thickness in cm.	Wavelength in Angstroms	Rotation in minutes	Field in gau·
32	1·504	5893	141	7170
32	1·210	5893	113	7150
28	1·504	5893	159	8060
do	do	5461	188	8090
do	do	4358	305	8070
do	1·210	5893	128	8100
do	do	5461	151	8080
do	do	4358	243	8060

$\frac{V_{5461}}{V_{5893}}$ = 1·184 (I.C.T.)
1·180 (Observed)
$\frac{V_{4358}}{V_{5893}}$ = 1·916 (I.C.T.)
1·92 (Observed)

TABLE II

Rock Salt (NaCl)

Crystal No.	Thickness in mm.	Field in gauss		λ 5893	λ 5461	λ 4358
1	4·18	8080	2ρ	238′	280′	470′
2	9·05	7160	2ρ	464′	546′	915′
			V	0·0355	0·0418	0·0705
			n	1·5443	1·5475	1·5606
			$\lambda\frac{dn}{d\lambda}$	0·0387	0·0454	0·0774
			γ	91·6%	92·1%	91%

TABLE III

Sylvine (KCl)

Field 8080 gauss

Crystal No.	Thickness in mm.		λ 5893	λ 5461	λ 4358
1	3·55	2ρ	162′	192′	321′
2	6·96	2ρ	278′	334′	550′
		V	0·0282	0·0334	0·0561
		n	1·4904	1·4932	1·5046
		$\lambda\frac{dn}{d\lambda}$	0·0331	0·0392	0·0662
		γ	84·6%	84·5%	84·7%

TABLE IV

Fluorspar (CaF_2)

Field 8080 gauss

Crystal No.	Thickness in mm.		λ 5893	λ 5461	λ 4358
1	10·32	2ρ	150′	176′	285′
2 (violet)	7·44	2ρ	108′	126′	
		V	0·00898	0·01049	0·01710
		n	1·43383	1·43495	1·43949
		$\lambda\frac{dn}{d\lambda}$	0·0140	0·0165	0·0260
		γ	63·6%	63·6%	65·2%

TABLE V

Lithium Fluoride (*LiF*)

Thickness in mm.	Field in gauss		λ 5893	λ 5461	λ 4358
27·27	7160	2ρ	343′	400′	635′
27·27	8080	2ρ	384′	450′	712′
		V	0·00876	0·01023	0·01620
		n	1·39260	1·39341	1·39724
		$\lambda\frac{dn}{d\lambda}$	0·01153	0·01341	0·02110
		γ	76·1%	76·3%	77·0%

TABLE VI

Potassium Bromide (*KBr*)

Field 8080 gauss

Crystal No.	Thickness in mm.		λ 5893	λ 5461	λ 4358
1	5·35	2ρ	343′	407′	696′
2	5·27	2ρ	338′	398′	693′
3	4·56	2ρ	295′	348′	601′
		V	0·0398	0·0469	0·0813
		n	1·5585	1·5631	1·5813
		$\lambda\frac{dn}{d\lambda}$	0·0538	0·0633	0·1104
		γ	73·5%	73·5%	73·2%

TABLE VII

Ammonium Chloride (NH_4Cl)

Field 8080 gauss

Crystal No.	Thickness in mm.		λ 5393	λ 5461	λ 4358
1	9·05	2ρ	544′	641′	1088′
2	3·16	2ρ	190′	223′	381′
3	2·52	2ρ	114′	134′	232′
		V	0·0367	0·0432	0·0743
		n	1·6397	1·6439	1·6621
		$\lambda\frac{dn}{d\lambda}$	0·0507	0·0595	0·1070
		γ	72·3%	72·7%	73·1%

TABLE VIII

Ammonium Bromide (NH_4Br)

Field 8080 gauss

Crystal No.	Thickness in mm.		λ 5398	λ 5461	λ 4358
1	4·11	2ρ	334′	397′	693′
2	2·67	2ρ	212′	250′	443′
		V	0·0499	0·0589	0·1045
		n	1·7157	1·7217	1·7478
		$\lambda\frac{dn}{d\lambda}$	0·0727	0·0857	0·1505
		γ	68·6%	68·8%	69·5%

TABLE IX

Periclase (MgO)

Field 8080 gauss

Crystal No.	Thickness in mm.		λ 5393	λ 5461	λ 4358
1	7·45	2ρ	403′	475′	778′
2	7·75	2ρ	421′	495′	816′
3	11·91	2ρ	660′	774′	1247′
4	13·35	2ρ	735′	867′	1418′
		V	0·0344	0·0405	0·0670
		n	1·7375	1·7410	1·7560
		$\lambda\frac{dn}{d\lambda}$	0·0426	0·0500	0·0847
		γ	80·8%	81%	79·1%

with sufficient accuracy in the fluorspar crystal having a violet fluorescence. This was due to the feeble transmission by the crystal towards the violet end of the spectrum.

4. Collection of Results and Discussion

The Verdet constant, refractive index and the magneto-optic anomaly of the eight crystals studied in this paper, together with the values for diamond and zincblende previously obtained by the author, are given in Table X.

Table X

Substance	n_{5893}	V_{5893}	γ %
ZnS ..	2·3683	0·226	91
NaCl ..	1·5443	0·0358	91
KCl ..	1·4904	0·0286	86
MgO ..	1·7375	0·0344	81
LiF ..	1·3926	0·00876	76
KBr ..	1·5580	0·0398	74
NH_4Cl ..	1·6397	0·0367	73
NH_4Br ..	1·7157	0·0499	69
CaF_2 ..	1·4338	0·00898	65
Diamond ..	2·4172	0·0233	28

Van Vleck (1932) has shown that atoms having the inert gas configuration must obey the unmodified Becquerel formula, *i.e.*, they should have a γ value of 100%. The lower value of γ for the well-known ionic substances NaCl and KCl may be attributed to the deviation of the electron atmospheres of the ions in the crystal from the inert gas configuration. It is natural to expect, on this basis, that in diamond which is completely a covalent crystal, the γ value should be very low. The low values of γ for NH_4Cl and NH_4Br may also be attributed to the covalent N–H bond. But a careful study of Table X shows that this elementary hypothesis cannot explain many of the facts observed. For instance, CaF_2 which is usually considered to be an ionic crystal has a value of γ considerably lower than the values for other ionic crystals. At the present stage it has not been possible to correlate any other physical property with the magneto-optic anomaly. Indeed to effect such a correlation, more data on the magneto-optic anomaly in crystals are necessary. Investigations on the determination of the values of γ in other ionic cubic crystals and their solutions are in progress, and it is expected that the results of these studies will throw some light on the meaning of the magneto-optic anomaly.

The author wishes to record his grateful thanks to Professor Sir C. V. Raman for the kind encouragement he gave during the course of this investi-

gation and for the loan of the crystals. Thanks are also due to Dr. R. S. Krishnan and Mr. K. G. Ramanathan for the loan of the crystals of ammonium chloride and bromide.

5. Summary

The paper records the Verdet constant, refractive index, dispersion and the magneto-optic anomaly of eight cubic crystals, *viz.*, NaCl, KCl, CaF_2, LiF, KBr, NH_4Cl, NH_4Br and MgO for the wavelengths, λ 5893, λ 5461 and λ 4358. The magneto-optic constants for the last five crystals mentioned above have been determined for the first time. The values of the Verdet constant for λ 5893 and the magneto-optic anomaly for these crystals are as follows:—LiF 0·00876, 76%; KBr 0·0398, 74%; NH_4Cl 0·0367, 73%; NH_4Br 0·0499, 69%; MgO 0·0344, 81%.

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ANTHRAQUINONE SERIES

Part I. 1-Aminoanthraquinone-2-aldazine

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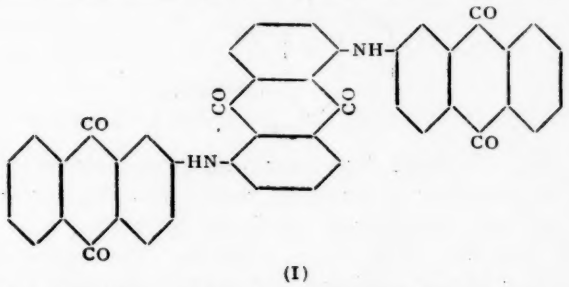
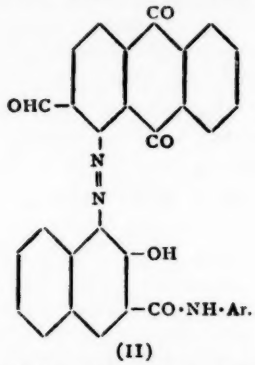
The anthraquinonoid vat colour, Indanthrene Bordeaux B, is stated in the literature[1] to be the trianthrimide (I) obtained by the condensation of one molecule of 1 : 5-diaminoanthraquinone with two molecules of 2-chloroanthraquinone. In the course of an examination of a series of acylaminoanthraquinones and anthrimides, which will be the subject of a later communication, the trianthrimide (I) was synthesised and found to be different



(I)

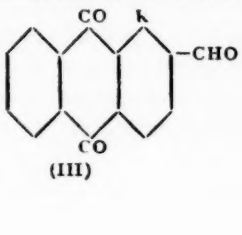
from Indanthrene Bordeaux B in its colour reactions and chemical properties. The trianthrimide (I) has also been mentioned as being identical with Indanthrene Claret B and later Anthra Claret RT[2]. The constitution of Indanthrene Bordeaux B as stated in the literature is therefore erroneous, and work was undertaken to determine the authentic structure of the dye marketed by the I. G. Farbenindustrie as Indanthrene Bordeaux B. Commercial Indanthrene Bordeaux B is a deep chocolate powder, which gives claret-red to bordeaux shades on cotton yarn from an intense olive green, alkaline hydrosulphite vat. Purified from diluents by boiling with 5% hydrochloric acid, it crystallised from nitrobenzene in red-violet needles, m.p. above 360°. The nitrogen content of the dye was found to be 6·4% by the micro-Kjeldahl method, and 11·0 by the micro-Dumas method. Since the normal Kjeldahl procedure is known to give low values in the case of compounds containing nitro, azo and certain other groups, the digestion was carried out in presence of reducing agents, but the lower value was always obtained.

Indanthrene Bordeaux B behaved as a primary amine, and gave diacetyl and dibenzoyl derivatives; treatment with *p*-toluenesulphonyl chloride gave, however, a mono-acyl derivative. The dye could not be diazotised with hydrochloric acid and sodium nitrite; but was readily diazotisable by the use of glacial acetic acid and concentrated sulphuric acid.[3] When the diazotised substance was coupled with Naphtol AS-TR and Naphtol AS-E, the azo dyes (II) were found to be identical with the corresponding



(II)

azo dyes from diazotised 1-aminoanthraquinone-2-aldehyde. Indanthrene Bordeaux B was unaltered by prolonged boiling with 20% alcoholic potassium hydroxide, and was substantially unaffected by boiling with concentrated hydrochloric acid for several hours. The dye was hydrolysed, however, by boiling with 2 vol. of sulphuric acid (sp.gr. 1·82) and 1 vol. of water, the isolable product being 1-aminoanthraquinone-2-aldehyde in a yield which indicated that it was the main component in the dye molecule. Treatment with concentrated sulphuric acid at 160° gave about a 30% yield of 1-aminoanthraquinone-2-carboxylic acid identical with the product obtained from 1-amino-2-cyano-anthraquinone by similar treatment.[4] A second product of hydrolysis, isolated in rather more than equivalent amount, was α-aminoanthraquinone, apparently formed by the decarboxylation of the 2-carboxylic acid. When Indanthrene Bordeaux B was deaminated by treating the diazonium sulphate with alcohol and copper sulphate, the product was anthraquinone-2-aldehyde (III; R=H), which was oxidisable



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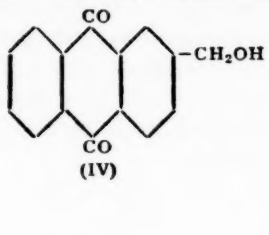


(IV)

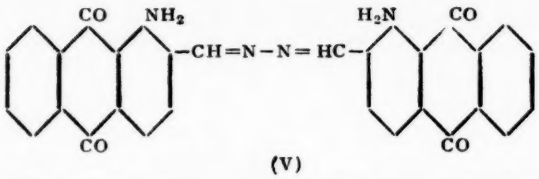
with chromic acid to anthraquinone-2-carboxylic acid. Reduction of the diazonium sulphate with formaldehyde[5] gave a mixture of anthraquinone-2-carboxylic acid and anthraquinone-2-carbinol (IV). By treatment of the diazo salt of Indanthrene Bordeaux B with cuprous chloride, 1-chloroanthraquinone-2-aldehyde (III; R=Cl) was obtained; oxidation of the latter with chromic acid led to 1-chloroanthraquinone-2-carboxylic acid. By hydrolysing the diazo salt of the dye with 50% sulphuric acid, 1-hydroxyanthraquinone-2-aldehyde (III; R=OH) was obtained. The formation of 1-substituted derivatives of anthraquinone-2-aldehyde and anthraquinone-2-carboxylic acid as degradation products indicated that Indanthrene Bordeaux B is a derivative of 1-aminoanthraquinone with a carbon link at the 2-position. The nitrogen content (by the Dumas method) corresponded to two nitrogen atoms for each anthraquinone ring. The acyl derivatives of the dye, however, accounted for only one amino group for each anthraquinone molecule, and the other nitrogen atom must therefore be attached to the 2-carbon atom in a form removable with relative ease after diazotisation of the 1-amino group.

It has been noticed by Fierz-David and Matter[6] that cyanuric acid derivatives gave low values for nitrogen by the Kjeldahl method. The possibility of Indanthrene Bordeaux B being the cyanurated dye, produced by the polymerisation of 1-amino-2-cyano-anthraquinone, was therefore considered, since this structure would adequately explain the analytical data and the products of hydrolysis; it was also conceivable that the molecule might break down on diazotisation and submission to the Sandmeyer reaction.

Trimeric 1-amino-2-cyanoanthraquinone has been mentioned in the patent literature as a violet compound of high m.p., soluble in concentrated sulphuric acid with an olive-brown colour and giving a violet shade from a dark violet vat.[7] The trimer, prepared with some difficulty, proved to be different from Indanthrene Bordeaux B.

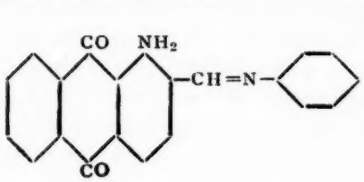
An alternative structure was the aldazine (V) obtainable by the action of hydrazine hydrate on 1-aminoanthraquinone-2-aldehyde (III; $R=NH_2$).

Synthesis of 1-aminoanthraquinone-2-aldazine (V).—1-Amino-2-methylanthraquinone,[8] prepared from 2-methylanthraquinone by nitration and reduction, gave on heating with nitrobenzene in presence of anhydrous potassium carbonate, 1-amino-anthraquinone-2-phenyl-azomethine (VI).[9] Acid hydrolysis of (VI) gave 1-aminoanthraquinone-2-aldehyde (III; $R=NH_2$),[10] which by the action of hydrazine hydrate led to the aldazine



(V)

(V),[9,11] identical in all respects with Indanthrene Bordeaux B. Alternatively the dye could be prepared by the action of hydrazine hydrate on anthraquinone-1 : 2-isoxazole (VII),[12] which was obtained by heating 1-nitro-2-methylanthraquinone with aluminium chloride. The second



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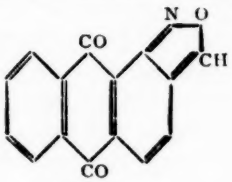
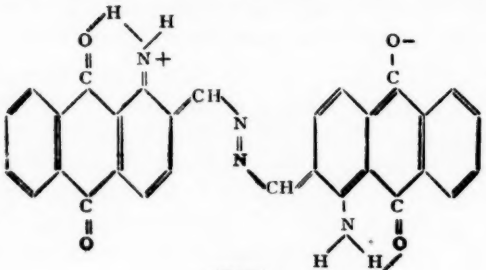


(VII)

method was more convenient, and gave a purer product. The isoxazole (VII) can also be prepared by the action of fuming sulphuric acid on 1-nitro-2-methylanthraquinone.[13]

The properties and behaviour of Indanthrene Bordeaux B may now be considered in the light of its constitution (V). The substance is deeply coloured, and has the requisite stability to alkaline reduction for application as a vat dye. The colour and stability of the compound must be associated with the resonance structures (VIII), (IX) and (X); the amino groups introduce the possibility of such resonance, since anthraquinone-2-aldazine is light yellow in colour and has no dyeing properties.[14] The features to be noticed in form (IX) are (*a*) the resonance in the two anthraquinone units which may also be postulated in α-amino-anthraquinone; and (*b*) the long and unbroken conjugation between the doubly bound oxygen atoms. On



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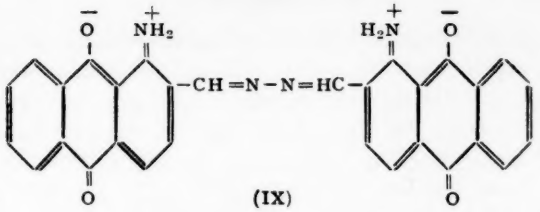

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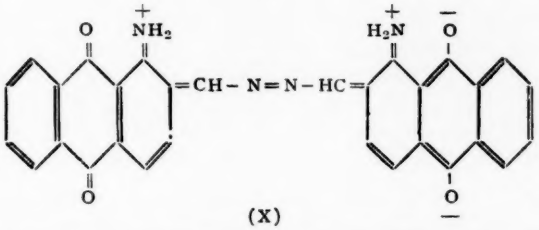

(X)

treatment with sulphuric acid and sodium nitrite, fission of the aldazine linkage takes place, together with diazotisation of the amino groups; as a result the azo dye obtained by coupling with a naphthol is identical with the azo dye from diazotised 1-aminoanthraquinone-2-aldehyde. For the same reason, attempts to deaminate Indanthrene Bordeaux B and to replace the amino groups by chlorine and by hydroxyl have led to anthraquinone-2-aldehyde and its 1-substituted derivatives. The formation of anthraquinone-2-carboxylic acid and anthraquinone-2-carbinol (IV) in the formaldehyde treatment referred to earlier, is the result of anthraquinone-2-aldehyde undergoing a Cannizzaro reaction.

Treatment of Indanthrene Bordeaux B with boiling concentrated sulphuric acid yields 1-aminoanthraquinone-2-carboxylic acid on account of the oxidation of 1-aminoanthraquinone-2-aldehyde, the product of hydrolysis, to the carboxylic acid under the conditions of the reaction.

In view of the sensitivity of Indanthrene Bordeaux B to the combined action of sulphuric acid and sodium nitrite, we have examined the behaviour of benzaldazine, and found that fission of the aldazine linkage takes place much more readily than with sulphuric acid alone. This is also true of Schiff's bases, the anil from aniline and benzaldehyde yielding diazobenzene sulphate smoothly and quantitatively, as determined by coupling with β-naphthol. The mechanism of these reactions is being examined. Franzen and Zimmermann[15] have recorded that by the action of ethyl nitrite on benzaldazine in presence of acetyl chloride in boiling benzene, benzaldehyde and benzaldehyde diethyl acetal were obtained.

Experimental

1 : 2′, 5 : 2″-*Trianthrimide* [1 :5-(2 :2′-*dianthraquinonyl*)-*aminoanthraquinone*] (I).—1 : 5-Diaminoanthraquinone (1 g., 1 mol.), 2-chloroanthraquinone (4·1 g., 4 mols.), anhydrous sodium acetate (1·5 g.), anhydrous copper sulphate (0·3 g.) and nitrobenzene (90 g.) were heated under reflux for 24 hours. The product was filtered while hot, washed with benzene and the residue was extracted with hot nitrobenzene (100 c.c.) to remove unreacted components, then washed with benzene, alcohol and hot water. The product (2·1 g.) was obtained in red-brown rectangular plates with metallic lustre. Recrystallised from nitrobenzene, the plates did not melt up to 340°. (Found: N, 4·1. $C_{42}H_{22}O_6N_2$ requires N, 4·3%.) The trianthrimide (I) was found to be different from Indanthrene Bordeaux B in its properties (Table I).

Table I

Dye	Appearance	Alkaline hydrosulphate vat	Acid vat	Colour in conc.		Shade on cotton	Fastness	
				Nitric acid	Sulphuric acid		Light	Chlorine
1 : 2′, 5 : 2″—Trianthrimide (I)	Red-brown plates	Yellowish-red	Brown-yellow	Red brown	Yellowish green	Bordeaux	7–8	5
Indanthrene Bordeaux B	Red-violet needles	Intense olive-green	Brown	Red	Olive brown	Claret red	6–7	4

Purification of commercial Indanthrene Bordeaux B.—The dye (20 g.) was added slowly with stirring to 5% hydrochloric acid (200 c.c.) and boiled for 30 minutes, stirring occasionally. The mixture was filtered while hot, and the red-violet residue (15 g.) was crystallised from nitrobenzene. The red-violet needles melted above 340°. (Found: micro-Dumas C, 72·8; H, 3·4; N, 11·0. $C_{30}H_{18}O_4N_4$ requires C, 72·3; H, 3·6; N, 11·2%.)

The nitrogen content of the dye by the micro-Kjeldahl method was 6·4%, which was increased but slightly (6·7; 6·5; 7·2) by the addition of reducing agents (cellulose; copper powder; hydriodic acid) to the digestion mixture.

Derivatives of Indanthrene Bordeaux B.—

Acetyl derivative.—The dye (1 g.) was warmed to 50° with acetic anhydride (5 c.c.), and the mixture was cooled to room temperature. Two drops of concentrated sulphuric acid were added to the mixture. The colour of the mixture at once changed from red to yellow and a clear solution

was obtained, which was shaken for 15 minutes and then poured into crushed ice. The brown-yellow precipitate (0·9 g.) was filtered and crystallised from acetylene tetrachloride. The minute yellow-brown needles did not melt up to 340° (Found: N, 8·9. $C_{34}H_{22}O_6N_4$ requires N, 9·5%). Acetylation could not be effected by means of acetic anhydride and pyridine.

Benzoyl derivative.—Indanthrene Bordeaux B (1 g.) was boiled with excess of benzoyl chloride (10 c.c.) and the mixture was cooled to 100°. Two drops of concentrated sulphuric acid were added, when hydrogen chloride was evolved and a clear red-brown solution resulted. Worked up as in the previous case, the brown precipitate (1·2 g.) was purified by dissolving in hot nitrobenzene, from which it separated as an amorphous powder, not melting below 340° (Found: N, 8·6. $C_{44}H_{26}O_6N_4$ requires N, 7·9%).

p-*Toluenesulphonyl derivative.*—The dye (2 g., 1 mol.), *p*-toluenesulphonyl chloride (3·8 g., 5 mols.) and nitrobenzene (25 c.c.) were refluxed for three hours. The violet solution was filtered hot, and the filtrate steam-distilled. The dark violet residue could not be crystallised, and was purified by extracting with benzene and alcohol. It did not melt up to 340° (Found: N, 7·9; S, 4·8. $C_{37}H_{24}O_6N_4S$ requires N, 8·5; S, 4·9%).

Coupling of diazotised Indanthrene Bordeaux B with Naphtol AS-TR.—

Azo dye (*II*).—Indanthrene Bordeaux B (2 g.) was boiled with glacial acetic acid (16 c.c.). The mixture was cooled to 5° C. and added slowly to a solution of sodium nitrite (2 g.) in concentrated sulphuric acid (14 c.c.). After 30 minutes the diazosulphate was diluted with ice-cold water (150 c.c.), and added slowly to an alkaline solution of Naphtol AS-TR (3 g.; 2·5 mols.) with mechanical agitation. After 30 minutes the greenish precipitate was filtered; on washing with 5% hydrochloric acid, the precipitate changed to red-brown in colour. Crystallised from acetylene tetrachloride, the orange needles melted at 253–54°; undepressed when admixed with the corresponding azo dye with 1-aminoanthraquinone-2-aldehyde (Found: N, 7·7; Cl, 6·3. $C_{33}H_{20}O_5N_3Cl$ requires N, 7·3; Cl, 6·1%).

Coupling of diazotised Indanthrene Bordeaux B with Naphtol AS-E.—

The dye (2 g.) was diazotised and coupled with Naphtol AS-E (2·2 g.; 2 mols.) as in the previous experiment. The red azo dye (2·6 g.) crystallised from chlorobenzene in red needles, decomposing at 280–82° (Found: N, 7·8; Cl, 6·6. $C_{32}H_{18}O_5N_3Cl$ requires N, 7·5; Cl, 6·4%).

Hydrolysis of Indanthrene Bordeaux B.—

(*a*) *With alkali.*—The dye (2 g.) was refluxed with 20% alcohol caustic potash (80 c.c.) for 48 hours. Diluted with water (200 c.c.) and filtered, the red-violet residue (1·9 g.) was found to be the original dye.

(*b*) *With concentrated hydrochloric acid.*—The dye (1 g.) was refluxed with concentrated hydrochloric acid (20 c.c.) for 2 hours. The mixture was cooled, diluted with water (100 c.c.) and filtered. The red-violet product was extracted with dilute ammonia, and the residue (0·9 g.) was again the original dye.

(*c*) *With sulphuric acid.*—(A) Indanthrene Bordeaux B (1 g.) was refluxed with sulphuric acid (two vols. of concentrated sulphuric acid and one of water) (200 c.c.) for two hours, cooled and the mixture was diluted with water (100 c.c.) and filtered. The red residue (0·9 g.) was extracted with dilute ammonia to remove any 1-aminoanthraquinone-2-carboxylic acid formed. The product (0·8 g.) crystallised from nitrobenzene in red needles, which melted at 233–34°, undepressed when admixed with 1-aminoanthraquinone-2-aldehyde. It gave an olive solution in concentrated sulphuric acid, which changed to intense blue on the addition of a drop of formaldehyde. It gave a green alkaline hydrosulphite vat, from which cotton was dyed a pale pink shade.

(B) Indanthrene Bordeaux B (1 g.) was heated with concentrated sulphuric acid (10 c.c.) at 160° for two hours. The yellow-brown solution was cooled and diluted with water (200 c.c.). The brown-red precipitate was collected and extracted with hot dilute ammonia. The ammoniacal filtrate was acidified with dilute hydrochloric acid, and the red brown precipitate (0·3 g.) crystallised from nitrobenzene. The red-brown needles melted at 295–96°; undepressed when admixed with 1-aminoanthraquinone-2-carboxylic acid.

Treatment of diazotised Bordeaux B with alcohol and copper sulphate.—The dye (5 g.) was diazotised as described earlier. The diazo solution was added to water (100 c.c.), and then to boiling alcohol (95%, 200 c.c.) containing copper sulphate (1 g.). The mixture was refluxed for two hours, cooled and diluted with water (500 c.c.). The pink precipitate was collected (4·0 g.). Crystallised from alcohol (Norit), the colourless needles melted at 188–89°; undepressed when admixed with anthraquinone-2-aldehyde (Found: C, 75·8; H, 3·1. Calc. for $C_{15}H_8O_3$: C, 76·3; H, 3·4%). The substance gave a bright yellow solution in concentrated sulphuric acid, and a bright olive-green alkaline hydrosulphite vat. The *phenyl hydrazone* melted at 242°, and the *oxime* at 238°.

The 2 : 4-*dinitrophenylhydrazone* crystallised from nitrobenzene in orange-red needles, m.p. 319–20°. (Found: N, 14·0. $C_{21}H_{12}O_6N_4$ requires N, 13·5%.)

On dissolving the aldehyde (0·5 g.) in acetic anhydride (5 c.c.) at 50°, cooling and adding two drops of concentrated sulphuric acid, a red solution was formed. It was shaken for fifteen minutes and poured into crushed ice. The pale yellow diacetate of (III; R=H) (0·6 g.) crystallised from glacial acetic acid in colourless rectangular plates, m.p. 142–43° (Found: C, 67·4; H, 4·8. $C_{19}H_{14}O_6$ requires C, 67·4; H, 4·1%).

Oxidation of (III; R=H).—The aldehyde (2 g.) was heated under reflux with glacial acetic acid (20 c.c.) for 30 minutes. Chromic acid (CrO_3) (10 g.) dissolved in 50% acetic acid (50 c.c.) was added to the boiling acetic acid solution during two hours. After the addition, the solution was refluxed for 2 hours more. On cooling pale yellow needles separated (1·6 g.). Recrystallised from acetic acid, the pale yellow needles melted at 292°; undepressed when admixed with anthraquinone-2-carboxylic acid, prepared by chromic acid oxidation of 2-methylanthraquinone.

Treatment of diazotised Bordeaux B with alkaline formaldehyde.—An alkaline-formaldehyde solution was prepared by dissolving caustic soda (20 g.) in ice-cold water (120 c.c.) and adding 40% formalin (15 c.c.). After 15 minutes, the diazo solution from 3 g. of the dye diluted with ice-water (200 c.c.), was added during half an hour with mechanical stirring, keeping the reaction mixture alkaline throughout. Agitation was continued for 30 minutes. On leaving in the refrigerator for 1 hour, the brown precipitate (2·7 g.) was filtered, extracted with hot and 10% sodium hydroxide solution (200 c.c.). The brown-red residue (2·2 g.) crystallised from acetic acid (Norit) in pink needles, m.p. 288–90°; undepressed when admixed with anthraquinone-2-carboxylic acid (Found: C, 70·6; H, 3·0. Calc. for $C_{15}H_8O_4$: C, 71·4; H, 3·2%). The acid is soluble in hot dilute ammonia, gives a yellow solution in concentrated sulphuric acid, and a brown-red alkaline hydrosulphite vat.

By diluting the acetic acid mother-liquor, after the separation of anthraquinone-2-carboxylic acid, a colourless precipitate (0·3 g.) was obtained, which crystallised from water. On recrystallisation from benzene, the laminar melted at 183°. Mitter and Banerjee[16] quote the same m.p. for anthraquinone-2-carbinol (IV). On heating the substance (0·1 g.) with 3:5-dinitrobenzoyl chloride (0·08 g.) and benzene (10 c.c.) for 2 hours, the dinitrobenzoate crystallised from benzene in pale yellow needles, m.p. 241–42° (Found: N, 6·9. $C_{22}H_{12}O_8N_2$ requires N, 6·5%).

1-*Chloroanthraquinone-2-aldehyde (III; R=Cl).*—The diazo solution from 5 g. of the dye was added drop by drop to a solution of cuprous chloride in 20% hydrochloric acid (50 c.c.) at 75°. After the addition of the diazo

salt, the mixture was boiled for 10 minutes and kept on a water-bath for 2 hours. The mixture was diluted with water (200 c.c.), and the pink precipitate (4·3 g.) crystallised from 80% alcohol (Norit). The pale orange needles melted at 197–98°; undepressed when admixed with 1-chloro-anthraquinone-2-aldehyde, obtained from 1-amino-anthraquinone-2-aldehyde by similar treatment (Found: C, 65·7; H, 2·9; Cl, 12·8. Calc. for $C_{15}H_7O_3Cl$: C, 66·1; H, 2·5; Cl, 13·1%).

1-*Chloroanthraquinone-2-carboxylic acid.*—The chloro compound (1 g.) was oxidised, as in the case of anthraquinone-2-aldehyde with chromic acid (5 g.) in acetic acid. The pale yellow product (0·6 g.) was crystallised from glacial acetic acid. The pale yellow needles melted at 270°, undepressed when admixed with 1-chloroanthraquinone-2-carboxylic acid prepared by the Sandmeyer reaction on 1-aminoanthraquinone-2-carboxylic acid (Found: Cl, 12·3. Calc. for $C_{15}H_7O_4Cl$: Cl, 12·4%).

1-*Hydroxyanthraquinone-2-aldehyde* (*III*; *R*=*OH*).—Indanthrene Bordeaux B (3 g.) was diazotised, and added to ice-cold water (100 c.c.). Excess of nitrous acid was neutralised by urea, keeping the temperature of the diazo solution below 10°. The diazo solution was added gradually to 50% sulphuric acid (200 c.c.) at the boil. The acid solution was then boiled for 15 minutes, cooled, diluted with water (500 c.c.). The brown yellow precipitate (2·8 g.) was collected and crystallised from aqueous acetic acid. The yellow needles shrank and melted at 244–45° (Found: C, 70.7; H, 3.9. $C_{15}H_8O_4$ requires C, 71·4; H, 3·2%). The substance dissolves in caustic soda and sodium carbonate solution and in ammonia with a red violet colour. The alcoholic solution gives a deep yellow-brown colouration with ferric chloride. It gives a yellow solution in concentrated sulphuric acid, and a red-brown alkaline hydrosulphite vat.

2: 4-*Dinitrophenylhydrazone of* (*III*; *R*=*OH*).—The hydroxy compound (0·3 g.) was dissolved in hot glacial acetic acid (10 c.c.) and 2: 4-dinitrophenyl hydrazine (0·2 g.) was added. The mixture was refluxed for 2 hours. The product crystallised from nitrobenzene in red-brown needles, m.p. at 326–27° (decomp.) (Found: N, 13·3. $C_{21}H_{12}O_7N_4$ requires N, 13·0%).

1-*Amino-2-cyanoanthraquinone.*—1-Amino-2-bromoanthraquinone (5 g.; 1 mol.), cuprous cyanide (2 g.; 1·35 mols.) and dry pyridine (25 c.c.) were heated under reflux for 24 hours in an oil-bath at 150°. The reaction mixture was filtered while hot. The residue (5·9 g.) was extracted with dilute ammonia at 50° repeatedly, till the extract was no longer blue in colour. The red-brown residue (3·9 g.) crystallised from chlorobenzene in orange

needles, which melted at 240–42° (Found: N, 11·0. $C_{15}H_8O_2N_2$ requires N, 11·2%).

Trimer of 1-*amino*-2-*cyanoanthraquinone*.—1-Amino-2-bromoanthraquinone (10 g.), cuprous cyanide (5 g.; 1·43 mols.) and dry pyridine (50 c.c.) were refluxed for 48 hours at 150°. The reaction mixture was filtered while hot. The residue was extracted with dilute ammonia, and then with hot chlorobenzene to remove both the bromo and cyanoanthraquinone. The residue (5·9 g.; 71·4% yield) was sparingly soluble in most of the organic solvents. It was purified by dissolving in hot, high-boiling pyridine bases (b.p. 238–40°). The deep violet substance did not melt up to 340° (Found: N, 11·2. $C_{45}H_{24}O_6N_6$ requires N, 11·2%). It gives an olive-brown solution in concentrated sulphuric acid, and a dark violet alkaline hydrosulphite vat, which dyes cotton a violet shade of moderate fastness (light 3; chlorine 2–3).

Synthesis of 1-*aminoanthraquinone*-2-*aldazine* (*V*).—

1-*Aminoanthraquinone*-2-*phenylazomethine* (*VI*).—1-Amino-2-methylanthraquinine (10 g.), nitrobenzene (60 g.) and anhydrous potassium carbonate (5 g.) were refluxed for 6 hours. The reaction mixture was filtered while hot. On cooling the red-violet substance was collected (4·2 g.). Recrystallised from nitrobenzene, the red-violet rods melted at 212° (*D.R.P.* 343,064 quotes the m.p. 212°) (Found: N, 8·7. Calc. for $C_{21}H_{14}O_2N_2$: N, 8·6%). It gives a brown solution in concentrated sulphuric acid, and yellow-green alkaline hydrosulphite vat, which dyes cotton a pale pink shade.

1-*Aminoanthraquinone*-2-*aldehyde* (*III*; $R{=}NH_2$).—The azomethine (VI) (2 g.) was refluxed with glacial acetic acid (40 c.c.) and hydrochloric acid (20 c.c.) for 1 hour. On cooling the reaction mixture, the brown-red residue was collected (0·9 g.). Crystallised from nitrobenzene, the brown red needles melted at 232–33° (*D.R.P.* 346,188 quotes the m.p. 233–34°). It dissolves in concentrated sulphuric acid with a brown colour, and gives an intense green alkaline hydrosulphite vat, which dyes cotton a pale pink shade.

1-*Aminoanthraquinone*-2-*aldazine* (*V*).—To a boiling solution of 1-aminoanthraquinone-2-aldehyde (2 g.) in glacial acetic acid (20 c.c.), a 50% aqueous solution of hydrazine hydrate (0·25 c.c.; 0·5 mol.) and glacial acetic acid (5 c.c.) were added; a red-violet product separated almost immediately, and the mixture refluxed for 2 hours. On filtering hot, the residue (1·6 g.) crystallised from nitrobenzene in red-violet needles, which did not melt below 340° (Found: N, 11·5. $C_{30}H_{18}O_4N_4$ requires N, 11·20%). It gives a pale olive-brown solution in concentrated sulphuric acid, which changes

to intense blue on addition of formaldehyde. It gives an intense olive-green vat, which dyes cotton a bright claret shade of very good fastness (light 6–7; chlorine 4). The substance proved to be identical in all respects with Indanthrene Bordeaux B.

The aldazine (V) from the azomethine (VI).—1-Aminoanthraquinone-2-phenylazomethine (1 g.) was boiled with glacial acetic acid (20 c.c.), hydrazine hydrate (0·3 c.c. of 50% aqueous solution) and glacial acetic acid (5 c.c.) added, and the mixture refluxed for 2 hours. The violet residue (0·7 g.) obtained by filtering the hot reaction mixture, could not be crystallised from nitrobenzene as in the previous experiment; but the substance gave the same colour reactions as (*V*). The bordeaux shade on cotton was different from the Indanthrene Bordeaux B shade.

Anthraquinone-1 : 2-isoxazole (VII).—1-Nitro-2-methylanthraquinone (3g.) was mixed with powdered anhydrous aluminium chloride (15 g.), and heated at 160–80° for 2 hours. After cooling, ice and hydrochloric acid were added, and the brownish yellow product (2·1 g.) was purified by dissolving in hot xylene, from which it separated in pure form. The substance did not exhibit a sharp m.p., but shrank at 220° and decomposed at 250–52° (Found: N, 5·6. $C_{15}H_7O_3N$ requires N, 5·6%).

The aldazine (V) from the isoxazole (VII).—The isoxazole (1 g.) was refluxed with glacial acetic acid (20 c.c.), 50% hydrazine hydrate solution (0·1 c.c.) added, the mixture refluxed for 2 hours. Filtered hot, the red-violet residue (0·7 g.) crystallised from nitrobenzene in red-violet needles, which melted above 340°. (Found: N, 10·9. $C_{30}H_{18}O_4N_4$ requires N, 11·2%). It was identical with 1-aminoanthraquinone-2-aldazine (V) in all respects.

Summary

1-Aminoanthraquinone-2-aldazine (V), prepared by the action of hydrazine on 1-aminoanthraquinone-2-aldehyde or anthraquinone-1 : 2-isoxazole, and identified as the commercial vat dye, Indanthrene Bordeaux B, undergoes an interesting series of degradations. The colour and stability of the dye molecule are due to resonance effects, and on diazotising the amino groups the molecule breaks down readily, yielding 1-substituted derivatives of 1-amino-anthraquinone-2-aldehyde. It has been noticed that other aldazines and anils undergo facile fission on treatment with sodium nitrite and sulphuric acid.

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